VOL. XIV. [OCTOBER, 1892.] No. 6.

AMERICAN

CHEMICAL JOURNAL.

Contribution from the Laboratory of General Chemistry, University of Michigan.

SOME REACTIONS WITH ACETOACETIC ETHER AND WITH SALICYLIC ETHER.

BY PAUL C. FREER.

In a paper published by me last year[1] I gave a number of reasons why, in my opinion, acetoacetic ether is to be regarded as the ester of β-ketobutyric acid, while the sodium salt of this same substance is the derivative of β-hydroxycrotonic ether. Since that time J. U. Nef,[2] in an exhaustive paper, rich in experimental facts, has concluded that the only interpretation of the evidence which he has accumulated is that under all circumstances, whether as the free acid or in its metallic derivatives, acetoacetic ether behaves as if it were an unsaturated β-hydroxy ester. Von Pechmann,[3] in discussing some reactions of formylacetic ether, demonstrated that the latter substance is β-oxyacrylic ether, $CHOH = CH - COOC_2H_5$, and, owing to the radically different behavior of β-oxyacrylic ether and its derivatives toward acetyl chloride, benzoyl chloride, and toward aniline, concludes that acetoacetic ether undoubtedly has the ketone formula. More recently Claisen[4] published a paper on the action of chlorcarbonic ester on sodium acetoacetic ether. In this he enters into an extended discussion of the same reaction which was studied by Nef, and comes to conclusions which differ from those of the latter author. I would, myself, scarcely venture to resume the discussion of this extremely voluminous subject, did it not seem to me that I can advance further experimental evidence to disprove one or two of the conclusions reached by Prof. Nef in his previous article. On page 58 of Nef's paper the statement appears that, "provided a direct exchange of sodium and bromine respectively alkyle takes place when halogenes, acid chlorides or alkylhalides react with sodium acetoacetic ether, then the corresponding reactions must take place much more energetically with the salts of the heavy metals such as copper, lead and mercury acetoacetic ether," and the author concludes from the facts that the sodium derivative of acetoacetic ether reacts with alkyl halides, bromine, and with acid chlorides in the cold, and with the greatest energy, while, for instance, the copper and lead salts do so only very slowly when heated with a solvent in sealed tubes at 130°, that an addition of the reagents in question to the sodium derivative takes place previous to the separation of the sodium halide. In order to discover whether phenomena similar to those observed with sodium acetoacetic ether take place with substances with which no such additive action is possible, I investigated the reactions of sodium salicylic ester. The latter substance and acetoacetic ether, provided the latter is β-hydroxycrotonic ether, are similarly constituted,[1] as a glance at the following formulæ will show:

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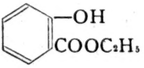
[1] This Journal **13**, 309.

[2] Ann. Chem. (Liebig) **266**, 52.

[3] Ber. d. chem. Ges. **25**, 1044.

[4] Ber. d. chem. Ges. **25**, 1760.



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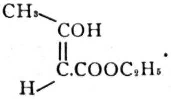

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Now, sodium salicylic ether reacts readily, in the cold, with benzoyl chloride, and does so with ethyl or methyl iodide when in alcoholic solution and slightly warmed on the water-bath, yet, in each of these cases, the substituting radicle is bound to oxygen, as is proven by the readiness with which it is split off by saponifying agents, so that the theory of addition is excluded in this case; furthermore, copper salicylic ether does not react at all under similar circumstances. Sodium salicylic ether in its physical characteristics is wonderfully similar to sodium acetoacetic ether.

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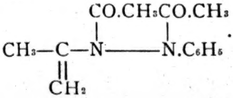
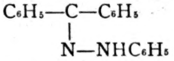
[1] Claisen, Ber. d. chem. Ges. **25**, 1780, also calls attention to this similarity. My work was completed previous to the publication of Claisen's article. The latter, however, publishes no experimental work on this point.

One of the chief reasons advanced by Nef in support of the theory that acetoacetic ether is β-hydroxycrotonic ether is the formation of β-phenylhydrazocrotonic ether by the action of phenylhydrazine on the former. The proofs advanced as to the constitution of this substance are, that it is readily oxidised to β-phenylazocrotonic ether by mercuric oxide, and that, when treated with acetyl chloride, it forms a substance which Nef regards as having the structure:



$$CH_3{-}\underset{\underset{CH_2}{\|}}{C}{-}\overset{\overset{CO.CH_3}{|}}{N}{-\!\!-\!\!-\!\!-}\overset{\overset{CO.CH_3}{|}}{N}.C_6H_5.$$

In studying the action of phenylhydrazine hydrochloride on acetoacetic ether I discovered that, in addition to 1-phenyl, 3-methyl, 5-pyrazolon, a substance melting at 36° is produced. The latter reacts readily when heated with methyl iodide, producing a thick syrup which, like antipyrin, is perfectly soluble in water. From this it follows, that at least one of the hydrogen atoms, which were attached to nitrogen in phenylhydrazine, is still present in the body melting at 36°. As I suspected that the oil which Nef obtained by the action of acetyl chloride on β-hydrazocrotonic ether might be identical with my low-melting solid, I repeated Nef's experiment and found that when β-hydrazocrotonic ether is treated with an excess of acetyl chloride, phenylmethylpyrazolon (which Nef overlooked), and an oil having the same boiling-point as that given by Nef, and identical with the boiling-point of my 36° melting solid, are produced. After repeated fractioning I obtained this oil in a solid form, it then melted at 36°, and was identical with the substance obtained by me from the action of phenylhydrazine hydrochloride on acetoacetic ether. The analysis of the pure substance, as well as the fact that it readily reacts with methyl iodide to form a body which is soluble in water, leaves no doubt that the formula assigned by Nef is incorrect. Although this experimental proof of the theory that the first product of the action of phenylhydrazine on acetoacetic ether is β-hydrazocrotonic ether is proven to be wrong, yet I have no doubt that the formula assigned to that substance by Nef is the correct one, from the following reasons. The phenylhydrazine derivatives of acetone and of acetophenone—two cases where the substances in question may have the formulæ $CH_3.COH=CH_2$ and $C_6H_5.COH=CH_2$,—are extremely unstable, when exposed to the air they are most readily oxidised, while benzoyl chloride, acetyl chloride, benzoic aldehyde, etc., readily decompose them in the cold. If benzoyl chloride is the reagent used, they separate phenylhydrazine hydrochloride, respectively dibenzoyl phenylhydrazine; on the other hand, the solid obtained by the action of phenylhydrazine on benzophenone, which is necessarily a hydrazone:  $\begin{array}{c} C_6H_5—C—C_6H_5 \\ | \\ N—NHC_6H_5 \end{array}$ is quite unchanged when exposed to the air and is not decomposed by benzoyl chloride.[1]

If acetoacetic ether is β-hydroxycrotonic ether, $CH_3.COH:CH.COOC_2H_5$, it should be capable of adding hydrobromic acid to form a tolerably stable addition-product; for aconitic acid, in which the carboxyl group, instead of hydroxyl, is attached to the β-carbon atom, reacts with hydrobromic acid to form bromtricarballylic acid. If acetoacetic ether, in ethereal solution, is treated with hydrobromic acid, even if the mixture is cooled with snow and salt, decomposition and the formation of carbacetoacetic ether takes place. On the other hand, if the ether is treated with exactly the calculated quantity of dry gaseous hydrobromic acid, a heavy oil is formed and the latter does not lose all of its halogen, even when repeatedly shaken with water, the product, after several washings, contains at least 10 to 12 per cent. of bromine; the latter is, however, completely removed by alcoholic potash and acetoacetic ether is regenerated. This hydrobromic acid addition-product, if it be such, is, however, extremely unstable. When allowed to stand, it decomposes, the liquid becomes dark in color and the usual decomposition-products of acetoacetic ether are formed. When treated with zinc ethyl no substances are formed, so far as I could discover, except high-boiling decomposition-products and regenerated acetoacetic ether. From these facts I am inclined to the opinion that this body is not a true hydrobromic addition-product in which hydrogen is attached to one carbon atom and bromine to the other. Were acetoacetic ether to have the ketone formula it is conceivable that hydrobromic acid could add as follows:

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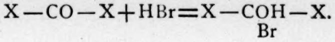
[1] The phenylhydrazide of acetone is readily oxidised by mercuric oxide, forming a deep red oil, from which, however, it has been impossible to separate a pure product, the hydrazone of benzophenone is very slowly attacked by mercuric oxide. Mr. Lichty is undertaking a study of these reactions in this laboratory.



$$\mathrm{X-CO-X+HBr=X-\underset{Br}{COH}-X.}$$

Such a body would, however, lose hydrobromic acid with the greatest ease.

One argument which has been repeatedly advanced against the hydroxyl formula of acetoacetic ether is that the latter substance does not react with acetyl chloride. I thought it of interest to study the action of the similarly constituted salicylic ether toward the same reagent, and found that it readily yielded acetyl salicylic ether. As yet, none of the advocates of the hydroxy formula of acetoacetic ether has explained why the hydroxyl group in that substance will not yield an acetyl derivative when treated with acetyl chloride; to my mind it should do so at least as readily as salicylic ether.

EXPERIMENTAL PART.

Sodium salicylic ether.—When salicylic ether is treated with metallic sodium, reaction at once sets in and the substance soon solidifies.[1] A better method for preparing this body is to dilute pure salicylic ether with about five times its own volume of dry toluene, and then to add sodium, which has been finely powdered under boiling toluene. The little pieces of sodium become covered with a layer of sodium salicylic ether, which prevents further action. The latter is very difficult to remove even by violent shaking of the flask, so that it is better not to wait for the end of the reaction, but to filter off the flaky sodium salicylic ether, dry on a porous plate, and separate the remaining pieces of sodium by means of a fine sieve. If salicylic ether is dissolved in a large quantity of dry ether, a concentrated solution of caustic soda then added, and the flask violently shaken, the sodium derivative will, after a little time, separate as an asbestos-like mass, which gradually, when dried, assumes a crystalline structure.

Sodium salicylic ether is a white solid which, when exposed to the air, has a pronounced odor of salicylic ether, due to the decomposition of the salt by moisture. Its solution in water has a strongly alkaline reaction and is partially decomposed with the separation of oily particles of salicylic ether. On addition of acids, unchanged salicylic ether separates from its sodium derivative.

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[1] Schreiner, Ann. Chem. (Liebig) **197**, 19.

0.7534 gram $C_9H_9O_3Na$ gave 0.2668 gram Na_2SO_4.

	Calculated for $C_9H_9O_3Na$.	Found.
Na	12.2 per cent.	11.5 per cent.

When sodium salicylic ether is suspended in dry chloroform and dry bromine is then added, reaction, accompanied by the separation of sodium bromide, at once sets in. The addition of bromine is continued until a permanent bromine color remains; the sodium chloride is then filtered and the clear chloroform solution evaporated. There remains a thick oil, which, however, soon becomes permeated with a mass of large, shiny crystals. After no more change takes place, the latter are filtered and recrystallised from dilute alcohol. The filtrate is unchanged salicylic ether, while the crystals, which are formed in a lesser quantity, consist of a dibrom-substitution-product of the latter. The formation of the free ether demonstrates that the bromine, when added, does not attack the sodium, but on the contrary takes the place of hydrogen, and that the hydrobromic acid so formed decomposes sodium salicylic ether, forming sodium bromide and salicylic ether.

1. $C_6H_4COOC_2H_5ONa + 4Br = C_6H_2Br_2COOC_2H_5ONa + 2HBr$.

2. $2C_6H_4COOC_2H_5ONa + 2HBr = 2C_6H_4COOC_2H_5OH + 2NaBr$.

This observation is entirely in accord with Nef's theory as to the action of bromine on sodium acetoacetic ether, that author believing that in the latter case addition of bromine first takes place, that this is followed by a separation of hydrobromic acid, and that the latter in turn forms sodium bromide and free acetoacetic ether. As a consequence this observation certainly supports the theory of the oxycrotonic ether formula for the sodium salt of acetoacetic ether

Dibromsalicylic ether.—Dibromsalicylic ether, formed as indicated above, crystallises from dilute alcohol in beautiful, shiny plates which have the appearance of mother-of-pearl. The substance dissolves in potassium hydroxide, and is separated therefrom unchanged by the addition of acids; it is even dissolved by a hot solution of sodium carbonate. The substance is with difficulty soluble either in cold or in hot water. When pure it melts at 100° to 101°.

0.1988 gram $C_9H_8Br_2O_3$ gave 0.2456 gram CO_2 and 0.0469 gram H_2O.

0.3196 gram $C_9H_8Br_2O_3$ gave 0.3709 gram AgBr.

	Calculated for $C_9H_8Br_2O_3$.	Found.
C	33.33 per cent.	33.69 per cent.
H	2.47	2.62
Br	49.53	49.37

When dibromsalicylic ether is heated with an excess of alcoholic potash on a water-bath for some hours it is completely saponified; when, after evaporating the alcohol and filtering, an excess of dilute sulphuric acid is added, dibromsalicylic acid separates as a white solid. This dibromsalicylic acid crystallises from dilute alcohol in white needles which melt at 225°, and is probably identical with the *m-m*-dibromsalicylic acid obtained by Lellmann and Grothmann.[1]

0.1558 gram $C_7H_4Br_2O_3$ gave 0.1997 gram AgBr.

	Calculated for $C_7H_4Br_2O_3$.	Found.
Br	54.05 per cent.	54.54 per cent.

Dibromsalicylic ether is changed to salicylic acid when treated for some time, in boiling dilute alcoholic solution, with an excess of sodium amalgam. Zinc dust and acetic acid have no effect, even when boiling.

The action of bromine on free salicylic ether results in the formation, not of a dibrom-, but of a monobrom substitution-product. If pure salicylic ether is dissolved in dry chloroform, and dry bromine, free from hydrobromic acid, is added, reaction begins slowly, and gradually increases in rapidity, although it at no time becomes violent. After an excess of bromine has been used and the evolution of hydrobromic acid has ceased, which takes place at the end of about twenty-four hours, the chloroform is distilled; the remaining oil, on cooling, crystallises in long needles which, after recrystallisation from nearly absolute alcohol, melt at 49° to 50°.

0.1814 gram substance gave 0.1394 gram AgBr.

	Calculated for $C_9H_{10}O_3Br$.	Found.
Br	32.4 per cent.	32.69 per cent.

Monobromsalicylic ether was saponified with alcoholic potash by heating on a water-bath for two hours; the alcohol was then distilled and the whole acidified. A white solid separates which, upon recrystallisation from dilute alcohol, forms colorless needles having a melting-point of 165° to 166°.

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[1] Ber. d. chem. Ges. **17**, 2728.

0.1852 gram substance gave 0.1627 gram AgBr.

	Calculated for $C_7H_5BrO_3$.	Found.
Br	36.86	37.5

This substance is undoubtedly the *m*-bromsalicylic acid obtained by Hübner and Heinzerling[1] by the action of bromine on free salicylic acid. The formation of the *m*-bromsalicylic ether by the action of bromine on salicylic ether seems, to my mind, to be an additional proof that at least one of the bromine atoms in the dibrom ether is in the meta position to carboxyl; but the reason why bromine forms a dibrom and not a monobrom ether, when it acts on the sodium derivative of salicylic ether, is not very apparent, although, possibly, the following explanation is the correct one. When bromine first acts on sodium salicylic ether it forms sodium monobromsalicylic ether and hydrobromic acid. The latter, however, instead of decomposing the former, attacks sodium salicylic ether to form free salicylic ether and sodium bromide. The bromine is now at liberty to once more substitute in the sodium derivative of the monobrom ether, converting the latter into sodium dibromsalicylic ether. According to this explanation, however, we would expect some monobromsalicylic ether to be formed during each reaction, but as yet I have not been able to discover such a body in the products produced.

Benzoylsalicylic ether.—If dry sodium salicylic ether is placed in a flask and covered with an excess of benzoyl chloride, reaction easily sets in in the cold and sodium chloride separates. The contents of the flask, after water has been added, are extracted with ether, the ethereal solution washed with sodium hydroxide solution, dried over calcium chloride, and evaporated. A white, crystalline solid remains which, after recrystallisation from dilute alcohol, forms small, flaky plates having a melting-point of 79° to 80°.

0.2225 gram substance gave 0.5780 CO_2 and 0.1071 H_2O.

	Calculated for $C_{16}H_{14}O_4$.	Found.
C	71.1	70.83
H	5.15	5.34

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[1] Zeitschrift für Chemie, 1871, 709.

Benzoylsalicylic ether is readily saponified when warmed for two hours with alcoholic potash. After evaporating the alcohol the whole is acidified and recrystallised from tolerably concentrated alcohol. By this means long needles separate; the latter melt at 156° and consist of salicylic acid. After filtering these crystals off the remainder is evaporated to dryness and then heated to boiling for about one hour, all of the salicylic acid being converted into phenol by this means. The decomposition-products which remain are extracted with sodium carbonate, the unchanged phenol separated by means of a wet filter, and the sodium carbonate solution acidified. A white crystalline solid precipitated, which, on recrystallisation, proved to be benzoic acid. Benzoylsalicylic ether is therefore decomposed into benzoic and salicylic acids by alcoholic potash; the benzoyl radicle is as a consequence undoubtedly attached to oxygen in this case, so that no addition-product could have been produced previous to the formation of benzoylsalicylic ether and yet *the reaction takes place readily and in the cold.*

The Action of Ethyl and Methyl Iodides on Sodium Salicylic Ether.

If dry ethyl iodide is added to perfectly dry sodium salicylic ether no reaction takes place, even on warming upon the water-bath. If, however, alcohol, in which substance sodium salicylic ether is soluble, is added, diethyl salicylic ether can readily be formed by gently heating for one or two hours, a method which is exactly like that employed in the production of alkylated derivatives of acetoacetic ether. After sodium salicylic ether in alcoholic solution has been boiled with ethyl iodide until a sample taken out and mixed with water no longer displays an alkaline reaction, the excess of alcohol and ethyl iodide is distilled, and the remainder, after the addition of water, is extracted with ether. After drying over calcium chloride the ether is evaporated, and the yellow-colored oil which remains is purified by fractional distillation. The diethyl salicylic ether so formed is a highly refracting, colorless oil which boils at 252°.[1] When boiled with alcoholic potash for two hours this substance is saponified, an oil separating on addition of acids. This oil when fractioned *in vacuo* boils at 228°, 110 mm. pressure, and when pure is a colorless, very highly refracting liquid. That this substance is in reality the ethyl ether acid is proven by the fact that it is readily hydrolised when heated in a sealed tube with concentrated hydrochloric acid, the product of this saponification being salicylic acid. An analysis of the ether-acid was not deemed necessary because of the similar reaction with methyl iodide; the methyl ether acid being a crystalline solid easily identified.

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[1] The boiling-point given by Fölsing, who prepared this substance from salicylic ethyl ether acid, is 251°.

The reaction with methyl iodide is like that with ethyl iodide; the ethylic salt of salicylic methyl ether acid being produced. This, when saponified by means of alcoholic potash, yields the potassium salt of the methyl ether acid, and the latter produces the free ether-acid when acidified. The acid crystallises from alcohol in large, transparent rods which melt at 98.5°, agreeing entirely with the descriptions of this substance previously given.[1] This methyl-ether acid is hydrolised with the greatest readiness by means of concentrated hydrochloric acid. Both methyl and ethyl iodide, therefore, with sodium salicylic ether, produce ethers in which the alkyl radicle is attached to oxygen; no addition could therefore have taken place, and yet the reaction is brought about with the greatest readiness.

In order, finally, to determine whether the compounds of the heavy metals with salicylic ether would react readily with alkyl iodides, copper salicylic ether was prepared and tested. Copper salicylic ether is easily formed by adding a solution of copper acetate to an alcoholic solution of sodium salicylic ether; it then separates as a green precipitate which can be filtered and dried. On addition of acids it regenerates salicylic ether. Now, copper salicylic ether shows no reaction with ethyl or methyl iodide even when boiled with the latter in the presence of alcohol, in which substance copper salicylic ether is slightly soluble. From these reactions it follows that the metallic derivatives of salicylic ether behave toward alkyl iodides exactly as do the similar ones of acetoacetic ether, so that in this case the supposed formation of intermediate addition-products cannot be advanced as an explanation of the ease with which sodium acetoacetic ether reacts with alkyl halides, while the salts of the heavy metals do not do so.

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[1] Graebe, Ann. Chem. (Liebig) **139**, 137, prepared the methyl ether acid and accurately described the same, as well as the ethyl ether of that body.

Acetyl salicylic ether.—Unlike acetoacetic ether, salicylic ether reacts with acetyl chloride. The ether is placed in a flask fitted with an inverted condenser, the upper extremity of which is closed by a mercury valve, a large excess of pure acetyl chloride added, and the whole boiled for some hours on a water-bath. The liquid is then poured into ice-water and extracted with ether. The ethereal solution is then repeatedly shaken with a tolerably concentrated solution of caustic soda, by which means any unchanged salicylic ether is separated, and it is then finally dried over calcium chloride. After evaporating the ether a thick oil remains, which is purified by fractional distillation. Acetyl salicylic ether boils at 272° and is very nearly colorless when pure.

0.2312 gram substance gave 0.5325 gram CO_2 and 0.1230 gram H_2O.

	Calculated for $C_{11}H_{12}O_4$.	Found.
C	62.80 per cent.	63.46 per cent.
H	5.77	5.90

Alcoholic potash very readily saponifies acetyl salicylic ether and forms salicylic acid.

The Action of Phenylhydrazine Hydrochloride on Acetoacetic Ether.

If a weighed quantity of acetoacetic ether is dissolved in alcohol and an equimolecular amount of phenylhydrazine hydrochloride is then added, reaction takes place slowly, in the same measure as phenylhydrazine hydrochloride is dissolved. After standing for twelve hours the change is complete. In order to isolate the products formed, the whole is poured into water and then repeatedly extracted with ether. This ethereal extract is washed, at first with water and finally several times with a dilute solution of sodium hydroxide. It is then dried over calcium chloride. After filtering, and evaporating the ether, an oil remains, which is best purified by repeated fractioning under diminished pressure. A small quantity which boils at 132° under ordinary barometric pressure has proved to be mesityl oxide. By far the larger portion,[1] however, boils at 202°, 32 mm. When this latter substance is cooled by means of snow and salt it solidifies. The solid so formed was purified by repeated solution in ice-cold absolute alcohol and precipitation by means of ice-water. It is then found to be a white, sandy, crystalline body which melts at 36° and which gives the following numbers on analysis:[1]

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[1] 7 grams for every 26 grams of acetoacetic ether and 28.8 grams of phenylhydrazine hydrochloride.

I. 0.1470 gram substance gave 0.3871 CO_2 and 0.1003 H_2O.
II. 0.1318 gram substance gave 0.3467 CO_2 and 0.0861 H_2O.
III. 0.1738 gram substance gave 0.4596 CO_2 and 0.1100 H_2O.
IV. 0.1815 gram substance gave 24.6 cc. N at 22° and 740 mm.
V. 0.1449 gram substance gave 19.8 cc. N at 21° and 730.5 mm.

	Found.				
	I.	II.	III.	IV.	V.
C	71.83	71.72	72.17	...	...
H	7.40	7.24	7.03	...	...
N	...	...	...	15.22	15.4

The substance used for analysis III was purified by conversion into the hydrochloride, recrystallising, liberating the base with pure potash, and once more recrystallising the latter.

The analytical data agree best with a formula of $C_{12}H_{14}N_2O$ which would require:

C	71.60 per cent.
H	6.99
N	14.

However, the nitrogen determinations give too high a result for such a substance, which would be phenylmethyl pyrazolon ($C_{10}H_{10}N_2O$) with an addition of C_2H_4. In order to throw some more light on the possible composition of this body, I prepared the hydrochloride by dissolving the solid melting at 36° in pure dry ether and then passing in dry hydrochloric acid. The hydrochloride separates as an oil, which rapidly becomes solid on rubbing with a glass rod and exposing to the air. The salt so obtained was dried over calcium oxide in a vacuum desiccator and gave the following results on analysis:

I. 0.3044 gram substance gave 0.1883 gram AgCl.
II. 0.3173 gram substance gave 0.1982 gram AgCl.

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[1] In a preliminary notice published by me (Journal für praktische Chemie **45**, 414) I gave an average of five analyses as follows: C, 69.41 per cent.; H, 6.55 per cent.; N, 15.32 per cent. As a result of these I made the statement that the oil was possibly an isomer of phenylmethyl pyrazolon. Since that time I have succeeded in crystallising this substance and, as will be seen above, the figures no longer agree with any such theory.

	Calculated for $C_{12}H_{14}N_2O.HCl$.	Found. I.	Found. II.
Cl	14.89	15.34	15.4

So far then as the present analyses indicate, the substance melting at 36° is nearest in composition to $C_{12}H_{14}N_2O$, and, although future investigation may show this body to be a mixture, I shall, for convenience, in the remainder of this paper designate it by that formula. One thing is certain, it has not the percentage composition of the diacetyl derivative of the phenylhydrazide of acetone, the formula assigned to the oil obtained by Nef by the action of acetyl chloride on β-phenylhydrazocrotonic ether, which oil I have obtained as a crystalline solid identical with the body melting at 36°, described above.

The substance $C_{12}H_{14}N_2O$ is a white, crystalline solid which is readily soluble in alcohol, chloroform and ether, insoluble in cold water. Its boiling-point is, when pure, 220° at 40 mm. pressure. The body is insoluble in alkalies, but dissolves readily in hydrochloric acid to form the hydrochloride described above. This hydrochloride is a white, crystalline solid which partly decomposes into the free base and hydrochloric acid when it is dissolved in water.

One gram of the substance $C_{12}H_{14}N_2O$ was dissolved in an excess of alcoholic potash, and boiled for three hours in a flask fitted with an inverted condenser. After evaporating the excess of alcohol and diluting with water, the whole was extracted with pure ether, dried over calcium chloride, and the ether evaporated. There remained 0.95 gram of an oil which solidified in a freezing mixture and proved to be the unchanged base. In order to see if concentrated sulphuric acid would have any effect, one gram was dissolved in an excess of that substance and, after allowing to stand over night, was warmed for some time at 50°, cold water was then added, the mixture rendered alkaline with a solution of sodium hydroxide, and extracted with ether. After drying over calcium chloride and evaporating the ether, 0.8 gram of unchanged substance remained. The loss of 0.2 gram may be due to some decomposition, but as yet I have not had an opportunity to reinvestigate the subject. The body $C_{12}H_{14}N_2O$ readily forms a dibrom addition-product when treated with pure bromine in absolute chloroform solution. This dibrom addition-product is a solid which crystallises in large, colorless prisms having a melting-point of from 111° to 112°.

In order to obtain some insight into the constitution of $C_{12}H_{14}N_2O$, the substance was heated with an excess of methyl iodide in a sealed tube for some hours at 100°. On opening the tube, evaporating the unchanged iodide, and removing iodine by means of molecular silver, a thick syrup remained, which was dissolved in water, filtered from a small quantity of an insoluble red solid, and evaporated to dryness. This operation was repeated until the product was perfectly soluble in cold water, when the whole was placed in a vacuum desiccator and put aside to crystallise. After standing for some weeks the substance had become only partially solid, so an attempt was made to fraction it *in vacuo*, but it was found that during this operation complete decomposition set in, with the formation of a basic oil which had the odor of pyridine. The formation of a soluble product by the action of methyl iodide on the body $C_{12}H_{14}N_2O$ reminds us very forcibly of the similar reaction of 1-phenyl-3-methyl-5-pyrazolon, and leaves no doubt in my mind that the two nitrogen atoms in the substance under consideration are present in exactly the same atomic relations as they are in that substance.

The alkaline extract of the original ethereal solution obtained from the action of phenylhydrazine hydrochloride on acetoacetic ether was exactly neutralised with hydrochloric acid, when a solid substance separated. The latter was repeatedly recrystallised from hot water, from which it separates in crystalline aggregates of concentric needles having a melting-point of 127°, and which from analysis proved to be 1-phenyl-3-methyl-5-pyrazolon. The identity of the latter was further confirmed by conversion into pyrazol-blue. Phenylmethylpyrazolon is the chief product of the reaction between phenylhydrazine hydrochloride and acetoacetic ether.

The Action of Acetyl Chloride on the Phenyl Hydrazide of Acetoacetic Ether.

The phenyl hydrazide of acetoacetic ether was prepared according to Nef's[1] method, and then an ethereal solution of the latter mixed with an excess of acetyl chloride and allowed to stand. Hydrochloric acid was evolved, and an oily layer separated at the bottom of the flask. The whole was then poured into ice-water and repeatedly extracted with alkalies, dried over calcium chloride and evaporated. A yellow oil remained, which, after fractioning *in vacuo*, was cooled in a freezing mixture. After the oil had solidified it was spread on a porous plate, and finally purified by dissolving in absolute alcohol and precipitating with ice-water. When so purified it melts at 36°, and has all of the properties of the solid melting at 36° obtained by the action of phenylhydrazine hydrochloride on acetoacetic ether. The alkaline extract of the ethereal solution was exactly neutralised with hydrochloric acid, when a solid separated, which, after recrystallisation, proved itself to be phenylmethylpyrazolon. The products of the action of acetyl chloride on the phenylhydrazide of acetoacetic ether are therefore identical with those obtained by the action of phenylhydrazine hydrochloride on the latter substance.

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[1] Ann. Chem. (Liebig) **266**, 170.

The Action of Hydrobromic Acid on Acetoacetic Ether.

Thirty-seven grams of acetoacetic ether were mixed with three volumes of perfectly dry ether cooled to —15°, and dry hydrobromic acid gas was passed in until the mixture was perfectly saturated. The whole was then allowed to stand over night, the ether was evaporated by passing a current of dry air through the contents of the flask. There remained a dark-brown oil which was fractioned; 9 grams passed over between 85° and 100°, 19.3 grams between 100° and 125°, 12.6 grams between 281° and 300°, and 6.6 grams between 330° and 360°. The lower fraction consisted of a mixture of ethyl bromide and alcohol and acetic ether. The fraction between 100° and 125° separated into two layers, the upper one of which contained acetone, alcohol and aqueous hydrobromic acid, the lower was ethyl bromide and acetic ether mixed with a high-boiling fraction. The fraction from 281° to 300° was carbacetacetic ether, while the one from 330° to 360° is as yet unidentified. Dry hydrobromic acid, in ethereal solution, therefore completely decomposes acetoacetic ether, its action being exactly parallel to that of hydrochloric acid.

Better results were obtained by the following means. A flask holding 12.5 liters was filled with dry hydrobromic acid gas, and after being placed in an open court during a very cold winter day, the calculated equimolecular quantity of acetoacetic ether (82.5 grams) was quickly poured in, the flask stoppered and allowed to stand for one hour at a temperature below 0°. The hydrobromic acid was almost completely absorbed, the stopper of the flask being pressed into the neck owing to the vacuum which had been created within. The product of the reaction was repeatedly shaken out with ice-water, the remaining heavy oil quickly dried over calcium chloride, and a bromine determination made.

0.1992 gram substance gave 0.0613 AgBr. Found Br = 13.09 per cent.

The results of a second determination were as follows: 0.2392 gram substance gave 0.0658 gram AgBr. Found Br = 11.7 per cent.

From these analyses it is evident that the major portion of the hydrobromic acid which was contained in the acetoacetic ether had been removed by the repeated washings with ice-water. On fractioning the oil which had been obtained, hydrobromic acid was given off and the oil separated into three portions; one, boiling from 70° to 100°, contained alcohol and ethyl bromide; the middle fraction, which was by far the largest, consisted of unchanged acetoacetic ether; while the highest-boiling one was carbacetoacetic ether. If the oil obtained after washing with ice-water is shaken with alcoholic potash, the hydrobromic acid is completely removed, and the product, with the exception of a little high-boiling substance, consists of unchanged acetoacetic ether. A similar result is obtained from the action of zinc ethyl on the dried oil containing hydrobromic acid. The hydrobromic acid addition-product of acetoacetic ether is therefore extremely unstable, and indeed, has much more of the character of a simple solution than of an additive product in which dissociation of the hydrobromic acid has taken place.

THE ATOMIC WEIGHT OF PALLADIUM.

BY HARRY F. KELLER AND EDGAR F. SMITH.

Two years ago[1] we showed that palladium can be completely precipitated by the electric current from a solution of palladodiammonium chloride in ammonia. In the same paper we expressed the belief that this behavior would afford an excellent means of determining the atomic weight of palladium, and we further stated that it was our intention to extend our investigation in this direction. Aside from the consideration that the atomic weight of every element should, if possible, be determined by more than one method, there were other reasons that led us to undertake a redetermination of this constant. The results published by different experimenters were few and discordant, and a critical examination of the methods employed by them seemed to show that the determinations were infected through various sources of error.

Berzelius was the first to determine the atomic weight of palladium. From his analysis of potassium palladous chloride, made in 1828,[2] the number 106.2 was deduced, which was generally conceded to be the most trustworthy, until Keiser in 1889,[3] by determining the amount of metal in palladammonium chloride, obtained the number 106.35.

That a high degree of accuracy cannot be claimed for Berzelius' number is evident, since he himself states that he did not succeed in completely dehydrating his salt without an appreciable loss of chlorine, and further, it is doubtful whether he succeeded in entirely eliminating the numerous impurities which occur in the commercial metal.

Keiser's value is the mean of two well-agreeing series of determinations which were apparently made with both skill and care; it is but slightly higher than that of Berzelius; both accord quite well with the position of the element in the periodic system. Nevertheless, we suspected that even these later determinations were not free from errors. Thus, we had found that Wilm's method, employed by Keiser in the preparation of his palladammonium chloride, does not give a product that is absolutely free from foreign metals, especially copper; and some observations made by us, while igniting the yellow salt, pointed to a probable loss of material during the reduction in hydrogen.

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[1] This Journal **12**, 212.

[2] Pogg. Annalen **13**, 455; Lehrbuch **3**, 1213.

[3] This Journal **11**, 398.

The value (Pd=111.88), calculated by Quintus Icilius[1] from his analysis of potassium pallado-chloride, differs so widely from the results of all other experimenters that it scarcely deserves serious consideration.

Preparation of Pallado-diammonium Chloride.

The crude palladium used in the preparation of the salt employed for the determination of the atomic weight was procured from the well-known firm of W. C. Heraeus in Hanau. It weighed about 28 grams and was in the form of foil. In a letter to one of us, Mr. H. Heraeus described the process by which it had been obtained, as follows:

Platinum ore is dissolved in aqua regia. After the insoluble residue has subsided, the clear supernatant liquid is drawn off and the platinum precipitated by ammonium chloride. The double salt is then separated from the mother-liquor and well washed. Filtrate and washings are united and mixed with metallic iron. The metals thereby thrown down are boiled with hydrochloric acid and dissolved in aqua regia, whereupon the precipitations by ammonium chloride and iron are repeated. After treatment with hydrochloric acid, the metals are again dissolved in aqua regia, the excess of the latter removed by evaporation and the residue taken up in dilute hydrochloric acid. Ammonia is now added to remove the iron, the solution warmed and filtered. From the filtrate the palladium is precipitated as palladammonium chloride. This salt is filtered off, washed, dried and ignited; the resulting metal being further purified by reconverting it into the yellow salt and then igniting the latter.

Mr. Heraeus also stated that the metal thus extracted is generally contaminated with copper and platinum. A qualitative examination showed that in addition to these, rhodium, gold, and iron were present in notable quantities.

To effect a removal of all these impurities the following process was, after some preliminary experiments, adopted:

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[1] Inaugural Dissertation, 1847.

The crude metal was dissolved in aqua regia, the excess of the latter removed by evaporation on the water-bath, and the residue digested with dilute hydrochloric acid. Everything passed into solution. After diluting with water, ammonia was added in excess and heat applied until the red palladammonium salt was dissolved. A reddish-brown precipitate, consisting of ferric hydroxide and a rhodium compound $[Rh_2(NH_3)_{10}Cl_6]$, remained; it was removed by filtration and the filtrate treated with an excess of hydrochloric acid; yellow palladammonium chloride was precipitated, and after the lapse of 48 hours this was filtered off with the aid of an air pump, thoroughly washed and drained. It was then redissolved in cold, dilute ammonia water[1] and separated from the small amount of the yellowish rhodium compound which remained undissolved. From the filtrate the palladammonium chloride was reprecipitated.

When dry, this salt was cautiously ignited in the air,[2] and the residual bluish-green mass then reduced in a current of hydrogen. The resulting metal was dissolved in aqua regia, the excess of which was afterwards expelled on the water-bath and by repeated evaporation with hydrochloric acid. The remaining chloride was then digested with water containing sufficient hydrochloric acid to dissolve it, and the solution carefully neutralised with sodium carbonate. The calculated amount of mercuric cyanide, dissolved in water, was next added: an immediate precipitation of yellowish palladous cyanide was produced. After this had been allowed to settle for several days in a warm place, the clear supernatant liquid was syphoned off. The precipitate was washed, first by decantation, then on the filter, and thoroughly drained with the air-pump. By ignition it was reduced to the metal, the highest heat of the muffle-furnace being maintained during four hours, to ensure the complete expulsion of any mercury that might have been present.

The resulting product was extracted with hydrochloric acid, to remove oxide of copper, and again dissolved in aqua regia. After repeated evaporations with hydrochloric acid, the diluted solution of palladous chloride was saturated with sulphur dioxide, whereby it assumed a bright yellow color; a slight precipitation occurred upon standing, appearing partly as a metallic mirror upon the sides of the flask, and partly in the form of dark flakes. It was found to consist of gold—by the purple of cassius test—and a trace of palladium. The addition of potassium sulphocyanate to the yellow solution produced a turbidity. The suspended particles were allowed to settle and recognised as the copper salt by the colors they imparted to the borax bead,—a strong blue in the oxidising flame, and a brick-red when treated with tin in the reducing flame.

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[1] Wilm, Ber. **15**, 241.

[2] In the ignitions of the salt in air we made observations similar to those recently described by Wilm (Ber. **25**, p. 220); we also found that not inconsiderable quantities of palladium are volatilised; a reddish-brown coating ($PdCl_2$?) was generally formed upon the lid and near the upper edge of the porcelain crucible. This may also explain the deposition of carbon upon the outside of the crucible.

Upon warming, the solution gradually returned to its original color, while a black precipitate separated out. When all the sulphur dioxide had been expelled by protracted boiling, the solution was filtered. What remained on the filter was soluble in nitric acid, and seemed to consist of palladium only, but was nevertheless consigned to the waste residues.

The bulk of the metal was now precipitated by warming the carefully neutralised filtrate with potassium formate. A turbulent evolution of carbon dioxide was observed, while the palladium came down in the form of a black powder. The precipitation was, however, not quite complete; the filtrate appeared yellowish, and gave upon treatment with more sodium carbonate and potassium formate an additional small precipitate which was likewise rejected.

The main precipitate of palladium was thoroughly washed and dried, transferred to a porcelain crucible, which was then covered and strongly ignited in the muffle for several hours.

The metal thus obtained had a slight tarnish, but became silver white when treated with hydrochloric acid. It weighed about two-thirds as much as the material with which we had started.

The conversion of the purified metal into palladammonium chloride was effected exactly as before described. It is scarcely necessary to mention that every precaution was observed to exclude particles of dust and filter-paper and to ensure complete washing of the salt. The adhering moisture was removed by successively placing the salt into a desiccator from which the air was then exhausted, subsequently into a steam-bath, and again into the vacuum desiccator over chloride of calcium and phosphorus pentoxide, for several weeks.

Analyses.

The perfectly dry salt was preserved in well-stoppered glass tubes. From these the different portions were rapidly transferred to the accurately weighed, silver-coated platinum dishes. The latter had never been used; they were carefully cleaned, however, to remove iron, etc. Their surfaces were smooth and even throughout. The silver deposits made from potassium-silver cyanide solution were in all cases quite uniform in appearance and perfectly white. The weights of these deposits lay between .2 and .4 gram. After washing with distilled water, the dishes were carefully dried in an oil-bath at a temperature of about 150°.

A Sartorius balance[1] of great accuracy and sensibility, and a set of carefully calibrated weights, by Westphal, were used for the weighings. The method of oscillations was employed, and great care taken to conduct the weighings under uniform conditions. The final adjustment with the rider was invariably made by each of us independently of the other, and the weighing repeated in case of disagreement.

Each series of experiments was made with a different preparation of the salt.

The first series consists of but three determinations:

I. 1.2996 grams of palladammonium chloride were dissolved in 30 cc. of pure ammonia water, the solution diluted with water to about 130 cc., and electrolysed in the cold with a current liberating 1 cc. electrolytic gas per minute. By raising the level of the liquid and thus exposing a fresh zone of silver, the completion of the precipitation was ascertained. The solution was now rapidly decanted and lukewarm water poured over the deposit. After a thorough washing, the dish was allowed to dry, first by placing it over chloride of calcium in a vacuum, subsequently by heating it in an atmosphere of carbon dioxide to 140° and again to 205°.

Weight of the silvered dish + Pd = 72.5274
Weight of the silvered dish = 71.8711

.6563

From this experiment we calculate the atomic weight to be 106.928.

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[1] We are indebted for the use of this instrument to the kindness of our friend Prof. John Marshall of this institution.

II. 1.0543 grams of the salt were treated exactly as in Exp. I.

Weight of the silvered dish + Pd = 62.33215
Weight of the silvered dish = 61.79962

.53253

By calculation the atomic weight is found to be 106.918.

III. The quantity of salt used in this experiment was 1.92945 grams. It was dissolved in 55 cc. of ammonia, diluted to 175 cc. and electrolysed with a current equivalent to 1.4 cc. of oxyhydrogen gas per minute. The deposit was washed with hot and with cold water. While yet moist it was placed in a desiccator connected with an air-pump and allowed to become dry. It was then heated in an oil-bath to 210°-215°. Carbon dioxide was not used in this experiment.

Weight of silvered platinum dish + Pd = 93.03165
Weight of silvered platinum dish = 92.05710

.97455

This result would place the atomic weight at 106.915.

Second Series.

I. 1.94722 grams of the yellow salt were dissolved in 50 cc. of ammonia water, diluted to 150 cc. and exposed for 18 hours to the action of a current liberating .8 cc. of electrolytic gas per minute. During the last hour the current was increased to 1.1 cc. of electrolytic gas per minute. The deposited metal was then washed with boiling water, dried *in vacuo*, afterwards at 110° for four hours, and finally for an hour at 150°. The weights remained constant.

Weight of silvered dish + Pd = 93.00283
Weight of silvered dish = 92.01940

.98343

The atomic weight 106.894 follows from this result.

II. 1.08649 grams of the substance were treated exactly as in the preceding experiment. The precipitated palladium was dried in an air-bath at 130° until constant weight was attained.

Weight of silvered dish + Pd = 72.65828
Weight of silvered dish = 72.10958

.54870

This corresponds to Pd = 106.885.

III. 1.28423 grams of substance were dissolved and electrolysed as in the two preceding cases. The washed deposit was treated for seven hours in an air-bath, the temperature of which was gradually raised from 110° to 150°, when the weight remained constant.

Weight of silvered dish + Pd = 62.64820
Weight of silvered dish = 61.99962

.64858

The resulting value is Pd = 106.890.

IV. The palladium salt employed for this determination weighed 1.68275 grams. It was treated in the same manner as described above.

Weight of silvered dish + Pd = 62.79500
Weight of silvered dish = 61.94490

.85010

This gives Pd = 106.955.

V. 1.69113 grams of the salt treated in the same manner gave the following result:

Weight of silvered dish + Pd = 73.18505
Weight of silvered dish = 72.33074

.85431

The calculated atomic weight of Pd = 106.949.

VI. 1.80805 grams of substance under the same conditions gave metal as follows:

Weight of silvered dish + Pd = 93.23320
Weight of silvered dish = 92.32010

.91310

Whence we deduce the value Pd = 106.896.

Results.

1st series:

Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	At. Weight.
1.29960 grams	.65630 gram	106.928
1.05430	.53253	106.918
1.92945	.97455	106.915
	Mean =	106.920

Maximum, ...	106.928
Minimum, ...	106.915
Difference, ...	.013

2d series:

Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	At. Weight.
1.94722 grams	.98343 gram	106.894
1.08649	.54870	106.885
1.28423	.64858	106.890
1.68275	.85010	106.955
1.69113	.85431	106.949
1.80805	.91310	106.896
	Mean =	106.911

Maximum, ...	106.955
Minimum, ...	106.885
Difference, ...	.070

The results of the two series combined give the mean value Pd = 106.914.

The calculations are based on H = 1, N = 14.01, and Cl = 35.37.

To ascertain whether the expulsion of the occluded hydrogen in the above experiments was complete, the following experiments were made:

In Experiment I, Series 2, the dish containing the palladium deposit was carefully heated over the flame of a Bunsen burner on a wide sheet of asbestos; while still hot it was transferred to a desiccator connected with an air-pump; the weight remained unaltered.

A strip of platinum was electrolytically coated with palladium, which was then washed with boiling water, dried and weighed. There was no appreciable decrease of weight when it had been successively heated to 110°, 125°, and 150°.

A piece of palladium foil, carefully weighed, was suspended as negative electrode in acidulated water. It absorbed much hydrogen, but returned to its original weight when heated to 110° and cooled in a vacuum desiccator.

To exclude dust during the depositions, the dishes were kept covered with closely-fitting glass plates.

The liquids from which the palladium had been precipitated were invariably tested with hydrogen sulphide after they had been acidified. Not the slighest change of color was observed in any case.

All deposits were regular and adhered firmly to the dishes; their color resembled that of the sheet metal, and they showed a velvet-like lustre.

The mean of our results differs from that of Keiser's by .563, or more than half a unit. In both cases the determinations were based upon the conversion of palladammonium chloride into the metal, and since the results obtained by each method agree quite satisfactorily among themselves, the cause of the discrepancy must be sought either in a difference in the degree of purity of the respective preparations employed, or in some constant error inherent in one or in both of the methods. Now it has already been thrown out in the introductory remarks to this paper that Keiser's value was probably affected by both causes. Whether, and if so to what extent this was actually the case, we have tried to ascertain by the experiments hereafter described.

It is evident from the observations we made during the purification of our palladium that the foreign metals cannot be completely eliminated by merely precipitating and reprecipitating the palladammonium salt. This fact, however, cannot be directly used as an argument in favor of our results, since Keiser's metal and ours had come from different sources and therefore did not necessarily contain the same impurities.

The firm of Eimer & Amend in New York supplied us with a sample of the palladium used by Keiser, which we have analysed with the following results:

	I.	II.	III.
Pd	94.46	93.92	94.84
Pt	...	0.50	0.41
Rh	...	...	1.45
Au	...	0.19	0.22
Cu	...	0.56	0.58
Fe	...	0.24	0.31
			97.81

Silver, lead and zinc were entirely absent. Owing on the one hand to the difficulty of effecting a complete precipitation of palladium by a single reagent (except hydrogen sulphide), and on the other to the persistent co-precipitation of small amounts of the impurities, the course of analysis became exceedingly complicated, and a loss of material was unavoidable. But while we do not claim for the above figures a very high degree of accuracy, the analyses prove conclusively that both Heraeus' and Eimer & Amend's metal had essentially the same composition.[1]

Thus it was shown that the palladammonium salt prepared by Keiser could not have been perfectly pure. That this is not the only source of error affecting his determinations will be seen from the following three series of experiments.

First Series.

Palladammonium chloride of the same preparation that had served for the electrolytic determinations was reduced by heating it in a current of hydrogen. The apparatus used for this purpose was constructed exactly as described by Keiser, and his mode of operating closely adhered to; *the substance had not been powdered.*

When heat was applied a slight decrepitation occurred and dark stains of palladium appeared in the tube, both in the immediate vicinity of the boat containing the substance and some distance away from it in the anterior part.

	Wt. of $Pd(NH_3Cl)_2$.	Wt. of Pd.	At. Wt.
1)	0.62955 gram	0.31743	106.542
2)	0.77270	0.38942	106.438
3)	0.83252	0.41918	106.240
4)	0.99055	0.49895	106.328

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[1] Although no quantitative analysis of Heraeus' palladium was attempted, the process of preparing our material afforded us an opportunity of judging of the relative amounts of the foreign metals, and we can safely assert that they did not materially differ from those obtained in the analysis of Eimer & Amend's sample.

Second Series.

The material here employed was prepared from the crude metal by Wilm's method, exactly as described in Keiser's paper. The two different preparations, which we will designate as A and B, were respectively obtained from Heraeus' and Eimer & Amend's palladium.

Both in this and the following series the reduction was effected in an apparatus of modified construction. In a large generator of the Norblad pattern, hydrogen was prepared from pure granulated zinc and pure dilute sulphuric acid. It was purified by treatment with the following substances in the order given: Alkaline solution of lead acetate, pumice soaked in silver nitrate, solution of silver nitrate in water, concentrated sulphuric acid, sticks of caustic potash, calcium chloride, chips of pure copper heated to cherry-redness, calcium chloride, and pieces of glass coated with phosphorus pentoxide. By means of three-way stopcocks we were enabled to replace by dry air or pure carbon dioxide the hydrogen in the reduction-tube. A Péligot tube containing concentrated strong sulphuric acid was placed at the further end of the apparatus to prevent the entrance of air and moisture.

The salt was reduced to a fine powder in an agate mortar; otherwise the process was conducted in the same manner as in Series 1. No decrepitation was observed in any of the experiments, but ill-defined gray stains in the anterior part of the tube indicated the volatilisation of palladium, which was further confirmed by the deep-red color with which these stains dissolved in aqua regia. Attempts to estimate the amount of loss thus incurred proved unsuccessful.

The experiments of this series resulted as follows:

	Wt. of Substance.	Wt. of Metal.	At. Wt.
	A.		
1)	1.02175	0.51468	106.332
2)	1.10325	0.55590	106.396
3)	0.66690	0.33590	106.310
4)	0.86840	0.43733	106.280
	B.		
5)	1.41430	0.71255	106.372
6)	1.15234	0.58050	106.346

Third Series.

The experiments of this series differed only from the preceding in that the salt prepared by our method was substituted for the less pure material. The results were as follows:

	Wt. of Substance.	Wt. of Pd.	At. Wt.
1)	0.96229 gram	0.48502 gram	106.452
2)	0.97804	0.49294	106.419
3)	0.94253	0.47517	106.510
4)	0.86090	0.43405	106.574

The fact that particles of the substance were projected from the boat during the heating satisfactorily accounts for the discrepant results of the first series. By *finely powdering* the yellow salt previous to its reduction—a precaution not mentioned by Keiser—this source of error was avoided, but it was then observed that the method is infected with a constant error—a loss of palladium through volatilisation. And since the determinations of Series 3 are distinctly higher than those of Series 2, it follows that the retention of impurities in the palladammonium chloride obtained by Wilm's method has likewise introduced a small but appreciable error.

We have thus shown that three sources of error have contributed to make Keiser's determination of the atomic weight too low.

We have also endeavored to determine the atomic weight of palladium by converting the palladammonium salt into the sulphide by heating it in a current of hydrogen sulphide.[1] The following results were obtained:

	Wt. Pd $(NH_3Cl)_2$.	Wt. PdS.	At. Wt.
1)	0.71699 gram	0.47066 gram	107.07
2)	1.31688	0.86445	107.07

While we regard these results as in a measure confirming those of our electrolytic determinations, we do not attach to them equal value.

MICHIGAN MINING SCHOOL.

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[1] Berichte **23**, 3373.

THE ELECTROLYTIC SEPARATION OF PALLADIUM AND PLATINUM FROM IRIDIUM.

BY EDGAR F. SMITH.

The electric current precipitates both palladium and platinum[1] from solutions of these metals in the presence of an excess of an alkaline phosphate and free phosphoric acid. Metallic iridium under similar conditions is not precipitated, and the experiments that follow show that in this way the separation of palladium and platinum from iridium may be effected without difficulty.

Palladium from Iridium.

1. To 15 cc. palladium solution (=0.1458 gram metallic palladium) were added 30 cc. of disodium hydrogen phosphate (sp. gr. 1.0358), 5 cc. free phosphoric acid (sp. gr. 1.47), and 150 cc. of water. A current liberating 1.2 cc. electrolytic gas per minute acted upon this solution during the night. The deposit of palladium was bright and metallic in appearance, as well as very adherent. It was washed with hot water. Its weight equaled 0.1466 gram. The deposit was not thrown directly upon the platinum cathode, but upon a silver-coated platinum dish. The quantity of iridium present with the palladium was 0.1200 gram.

2. To 15 cc. palladium solution (=0.1458 gram of metallic palladium) were added 10 cc. of an iridium solution (=0.1200 gram of metallic iridium), 40 cc. of disodium phosphate (sp. gr. 1.0358), 5 cc. of free phosphoric acid (sp. gr. 1.47), and 200 cc. of water. The current that acted during the night upon this solution liberated 2 cc. of electrolytic gas per minute. The deposited metal was quite adherent and was washed with hot water. It weighed 0.1449 gram.

3. A current liberating 3 cc. of electrolytic gas per minute acted for 12 hours upon the following mixture: 10 cc. palladium solution (=0.1303 gram of metallic palladium), 50 cc. disodium phosphate (sp. gr. 1.0358), 5 cc. phosphoric acid (sp. gr. = 1.47), 10 cc. iridium sodium chloride solution (=0.1200 gram of

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[1] This Journal **13**, 206.

metallic iridium), and 250 cc. of water. The precipitated palladium weighed 0.1305 gram.

4. The conditions in this experiment were exactly like those in 3. The palladium deposit weighed 0.1299 gram.

5. With conditions similar to those in 3 and 4, the precipitated palladium weighed 0.1298 gram.

6. In this experiment the quantities of the substances and the volume of the liquid were the same as in 3, 4 and 5, but the current registered 3.1 cc. electrolytic gas per minute. The precipitated palladium weighed 0.1303 gram.

The palladium was precipitated, in the preceding experiments, either upon copper-plated or silver-plated platinum dishes. The latter were found to answer better for this purpose because the precipitated palladium was washed with hot water and during the process of drying there was no danger that the silver-coating would oxidise, which may readily happen with the copper in using copper-plated vessels. When the latter are used the metal deposit should first be washed with water, and this then displaced with absolute alcohol, although the latter is apt to loosen thin films of the precipitated metal.

Platinum from Iridium.

The ease and accuracy with which palladium was separated from iridium left little question but that platinum and iridium would behave similarly. The following results prove it:

1. A current liberating 1.8 cc. of electrolytic gas per minute acted during the night upon 0.1042 gram of platinum and 0.1200 gram of iridium in the presence of 40 cc. disodium phosphate, 5 cc. phosphoric acid and 200 cc. of water. The precipitated platinum weighed 0.1048 gram. It was bright and metallic in appearance, as well as very adherent. It was washed with hot water.

2. The conditions here were precisely the same as those described in 1. The precipitated platinum weighed 0.1052 gram.

3. In this experiment the current gave 1.4 cc. electrolytic gas per minute, otherwise the conditions were the same as in 1 and 2. The platinum deposit weighed 0.1035 gram.

4. The solution electrolysed contained 200 cc. of water, 50 cc. of disodium phosphate, 3 cc. of phosphoric acid, with the same quantities of metal as before, while the current liberated 2 cc. of

electrolytic gas per minute. The precipitate of platinum weighed 0.1046 gram.

5. The conditions were like those in 4, except that the current generated 1.6 cc. of electrolytic gas per minute. The weight of the precipitated platinum equaled 0.1042 gram.

The platinum metal, in these separations, was deposited upon silver-coated platinum dishes.

Rhodium is another member of the platinum group of metals that has been completely precipitated[1] by the current from an acid phosphate solution.

Numerous trials were made to separate it in this manner from iridium, and although the results were apparently accurate enough for quantitative purposes, a careful examination of the precipitated rhodium disclosed the presence of iridium, and in some instances, when the separation seemed very satisfactory, unprecipitated rhodium was discovered in the iridium solution. For the present it seems best not to publish the results that were obtained.

In the presence of an excess of sodium formate, iridium is not precipitated by a current yielded by ten Crowfoot cells. This is also true if an alkaline sulphocyanide be added to its salt solutions. It is in this and other directions that it is hoped a method will yet be found for the separation of iridium from rhodium.

The material necessary for the study of the electrolytic behavior of the platinum metals was furnished the writer by the gentlemen constituting the Council of the Am. Assoc. for the Advan. of Science. He would here tender them his sincere thanks for their liberality, and also acknowledge his indebtedness to Mr. D. L. Wallace for his constant and valuable aid in the preparation of the pure salts for this research.

CHEMICAL LABORATORY, UNIVERSITY OF PENNSYLVANIA, *June* 27, 1892.

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[1] Jr. Analyt. and Applied Chemistry **5**, 201.

ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.

BY H. N. STOKES.

If a little powdered anhydrous aluminium chloride be added to some ethyl trichlorsilicate, $SiCl_3(OC_2H_5)$, which is cooled by ice, it dissolves, but no reaction is observed; on removing from the ice, bubbles of gas soon appear, and the reaction often becomes violent, attended by heating of the liquid. The gas, which burns with green-edged flame and formation of hydrochloric acid, is obviously ethyl chloride. If now the liquid be gently heated it gradually becomes thick, then solid, and finally the entire amount of aluminium chloride sublimes unchanged.

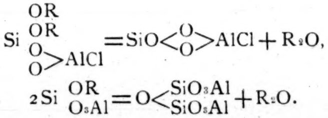
If instead of trichlorsilicate, tetraethylsilicate, $Si(OC_2H_5)_4$, be used, the reaction is in many respects the same, including the formation of ethyl chloride and the thickening of the liquid; but if the test-tube be connected with a condenser, it is seen that much ethyl ether is also produced. It may also be noticed that a relatively much greater amount of aluminium chloride than in the first case is required to produce the solid residue, while, unless a very considerable quantity has been added, none sublimes out on further heating.

It will be shown below that the action of the aluminium chloride on the trichlorsilicate is a case of so-called *catalytic action* (this being defined as a change brought about by a substance which at the end remains unaltered), while its action on the tetraethyl ether is one which is purely proportional to the relative amounts of the reagents, the aluminium remaining finally in combination with silica. It will also be seen that the monochlorsilicate, $SiCl(OC_2H_5)_3$, is intermediate in its behavior, a mere trace of aluminium chloride being sufficient to carry the decomposition to an end, when all the aluminium is found in fixed form. From these observations may be deduced the explanation of each case, including the catalytic action of the chloride on the trichlorsilicate. The details of the experiments, which were roughly quantitative, will be found in a separate section.

The only hypothesis which explains the facts observed is that in each case the substances react in a truly chemical sense, ethyl chloride and aluminium silicate compounds, Si—O—Al, being formed, but that in case of the chlorsilicates these bodies are exceedingly unstable, and decompose at once with regeneration of aluminium chloride, which is thus able to act again, and thus produce total decomposition when present even in traces.

The cause of this regeneration I take to be due, in part at least, to the tendency of the silicon to monopolise the oxygen, at the expense of the aluminium, forming Si═O, Si—O—Si, etc., whereby the metal is unable to remain combined with oxygen as long as this tendency of the silicon is not fully satisfied. If it happens that the latter is partly combined with chlorine (silicon chlorine), it at once exchanges it for an equivalent of oxygen. This, however, holds only in the aliphatic series of ethers, and in those cases where the chlorine is not the only constituent of the silicon compound. As I shall show elsewhere, silicon, when completely saturated with chlorine, as in silicon tetrachloride, does not show this tendency, neither does it exist in case of the aromatic silicates. From the latter, aluminium chloride, if in excess, takes all the oxygen and the silicon becomes completely chlorinated.

The formation of *ethyl ether* I can explain only by assuming in silicon a well-known property of carbon, which is manifested in the ortho-ethers of carbonic and other organic acids, namely, that the highest basicity is shown only when all the basic radicals are organic, while the metallic salts are of a lower degree of saturation, and the mixed organic metallic ortho-salts are so unstable as to be scarcely capable of existing under ordinary conditions. Assuming this analogy to exist, we should expect to find transformations like the following occurring:



$$\mathrm{Si}\begin{array}{l}\mathrm{OR}\\ \mathrm{OR}\\ \mathrm{O}\\ \mathrm{O}\end{array}\!\!>\mathrm{AlCl} = \mathrm{SiO}<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{AlCl} + \mathrm{R_2O},$$

$$2\,\mathrm{Si}\begin{array}{l}\mathrm{OR}\\ \mathrm{O_3Al}\end{array} = \mathrm{O}<\begin{array}{l}\mathrm{SiO_3Al}\\ \mathrm{SiO_3Al}\end{array} + \mathrm{R_2O}.$$

Strictly speaking, the tendency is not to form, as in the case of carbon, meta compounds containing Si═O, the analogue of carbonyl, but groupings in which two silicon atoms are united by oxygen, Si—O—Si, or $(\mathrm{SiO})_x$. This tendency is so strong, as has been pointed out by others,[1] that it is obviously the explanation of the fact that nearly all silicon compounds containing the analogue of carbonyl are not volatile, or volatile only at high temperatures, when by analogy with carbon, the reactions producing them should give volatile bodies of low molecular weight. This tendency to condensation and polymerisation by means of oxygen is the rule in the silicon series, and forms one of the most marked differences in the chemical behavior of these two elements, and the chief obstacle to producing by any simple means definite derivatives of silicic acid. I wish to be distinctly understood, therefore, as using the following formulas and equations only as typical ones reduced to the simplest possible form, the actual ones being vastly more complex and of almost infinite variety. Where R is used it stands, for sake of simplicity, for ethyl. That the quantitative experimental results do not conform with absolute strictness to the theoretical explanation is not surprising, for aluminium chloride is an extremely reactive body, tending to produce all sorts of secondary changes, while it is not to be expected that the transformations could be carried quantitatively to an end by heating the viscous and finally solid masses which result.

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[1] *e. g.* Mendelejeff, Grundlagen der Chemie, deutsch. Aufl. 767.

Ethyl trichlorsilicate, $SiCl_3(OR)$, is readily and completely decomposed by aluminium chloride, and the reaction is quite independent of the amount used, even a trace being sufficient. The products are ethyl chloride, free from ethyl ether, free aluminium chloride unchanged in amount, and finally a solid residue of the empirical composition $SiO.Cl_2$, but which in reality consists of a mixture of all sorts of complex silicon oxychlorides with free silica, the general result being expressed by the equation

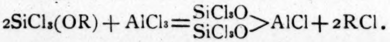
$$SiCl_3(OR) + xAlCl_3 = SiO.Cl_2 + RCl + xAlCl_3,$$

a typical case of catalytic action.

These oxychlorides are for the most part not volatile, but undergo at a high temperature transformation into oxychlorides richer and those poorer in chlorine,[1] the result being that they lose weight on ignition. The reactions by which they can be formed in the present case are very numerous, and only a few typical ones are given. The first steps in the process are

$$SiCl_3(OR) + AlCl_3 = SiCl_3.OAlCl_2 + RCl,$$

or



$$2SiCl_3(OR) + AlCl_3 = \begin{matrix} SiCl_3O \\ SiCl_3O \end{matrix}\!\!>AlCl + 2RCl.$$

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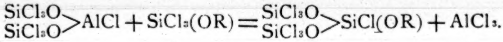
[1] Troost and Hautefeuille, Ann. chim. phys [5], 7, 469.

These bodies, being for reasons above given very unstable, at once react with fresh portions of trichlorsilicate,

$$\mathrm{SiCl_3.O.AlCl_2 + SiCl_3(OR) = SiCl_3.O.SiCl_2(OR) + AlCl_3},$$

and



$$\begin{matrix}\mathrm{SiCl_3O}\\ \mathrm{SiCl_3O}\end{matrix}\!>\mathrm{AlCl} + \mathrm{SiCl_3(OR)} = \begin{matrix}\mathrm{SiCl_3O}\\ \mathrm{SiCl_3O}\end{matrix}\!>\mathrm{SiCl(OR)} + \mathrm{AlCl_3}.$$

The regenerated aluminium chloride acts further, thus:

$$\mathrm{SiCl_3.O.SiCl_2(OR) + AlCl_3 = SiCl_3.O.SiCl_2.O.AlCl_2 + RCl},$$

which latter repeats the process, or may decompose thus:

$$\mathrm{SiCl_3.O.SiCl_2.OAlCl_2 = SiCl_3.O.SiO.Cl + AlCl_3},$$

and so on in every possible way *ad infinitum*, the aluminium chloride being continually regenerated, while the tendency of silicon to such condensations leads to increasing size of the molecules, which tend to the limit $(\mathrm{SiO.Cl_2})_x$, but seldom reach it before a high degree of complexity is attained. The increasing viscosity of the liquid interferes with the complete conversion of RO into RCl at a temperature below which other changes set in, which are manifested by more or less evolution of hydrochloric acid and gaseous hydrocarbons, with some carbonisation. There is, however, always an excess of silicon chlorine, which regenerates aluminium chloride, enabling it to act in minute amounts, and to reappear unchanged at the end.

It may be objected that these reactions are purely hypothetical, and that no such compounds as $\mathrm{SiCl_3.O.AlCl_2}$ have been shown to exist. In the following cases it will be shown that there is strong evidence of their existence, the aluminium being caught in the act, so to speak, and found ultimately, not as chloride, but in combination with oxygen.

Ethyl monochlorsilicate, $\mathrm{SiCl(OR)_3}$.—Aluminium chloride, in acting on this compound, produces a similar series of changes, even if used in relatively small amount, with this difference, that as there is not enough silicon chlorine to carry the regeneration through to the end, the aluminium remains finally as $\mathrm{Al_2O_3}$, and probably also as AlCl, combined with silica. The process is also complicated in certain cases by the formation of ethyl ether, which was explained above.

If we suppose the aluminium chloride to act by contact or influence merely, the decomposition would be expressed by the equation

$$SiCl(OR)_3 + xAlCl_3 = SiO_2 + RCl + R_2O + xAlCl_3,$$

and the result would be practically independent of the amount of chloride used, which could be finally recovered unchanged. It is found, however, that while a mere trace is sufficient to bring about total decomposition in nearly the sense of the last equation, by increasing the amount more ethyl chloride and less ethyl ether are formed; when a certain proportion is reached, the ethyl ether vanishes, and also up to this point all aluminium remains fixed in the residue. If more than this amount of chloride be taken, some remains unchanged, and may be recovered by sublimation. We may consider three distinct cases, with differing proportions of the reagents, namely, when

$$Si : Al \begin{cases} > 3 : 2 & (1) \\ = 3 : 2 & (2) \\ < 3 : 2 & (3) \end{cases}$$

The first case includes that where aluminium chloride is present only in traces, when the complete reaction, reduced to the simplest form and neglecting aluminium, would be

(*a*) $$SiCl(OR)_3 = SiO_2 + RCl + R_2O.$$

By increasing the proportion of chloride we have, for example,

$$20SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_{20}(Al_2O_3) + 26RCl + 17R_2O,$$
$$6SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_6\,(Al_2O_3) + 12RCl + 3R_2O, \text{ etc.}$$

It will be noticed that the relative amount of R_2O decreases and that of RCl increases as we approach the ratio Si : Al $= 3 : 2$. Reaching this point, which is case (2), we have

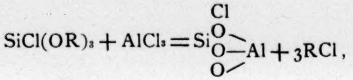
(*b*) $$3SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_3(Al_2O_3) + 9RCl.$$

The experiment shows that with this ratio no R_2O is formed, and that all aluminium remains in fixed form in the residue. Any further increase in the proportion of chloride belongs under case (3), where Si : Al $< 3 : 2$. For example, if the ratio be that of equality, or 3 : 3, we might have

(*c*) $$3SiCl(OR)_3 + 3AlCl_3 = (SiO_2)_3(Al_2O_3) + AlCl_3.$$

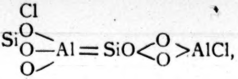
In fact, when this proportion is taken, unchanged aluminium chloride sublimes out of the residue. Owing, however, to the tendency of the silicon to monopolise the oxygen or to take the metasilicate form, this proportion admits of another reaction :

(*d*)



$$\mathrm{SiCl(OR)_3 + AlCl_3 = Si}\begin{array}{l}\mathrm{Cl}\\ \mathrm{O}\diagdown\\ \mathrm{O-Al}\\ \mathrm{O}\diagup\end{array}\mathrm{+\,3RCl},$$

and



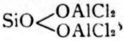
$$\mathrm{Si}\begin{array}{l}\mathrm{Cl}\\ \mathrm{O}\diagdown\\ \mathrm{O-Al}\\ \mathrm{O}\diagup\end{array}\mathrm{= SiO}{<}\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}{>}\mathrm{AlCl},$$

the residue being a chloraluminium metasilicate, or at least some similar form in which the preference of silicon for oxygen before chlorine is satisfied. The chlorine and aluminium in this form are practically fixed, as such a body as this would probably give off aluminium chloride, if at all, only at a high temperature, the effect being that the volatile chloride falls below the theoretical amount required by equation (*c*).

Finally, if Si : Al = 1 : 2—

(*e*) $$\mathrm{SiCl(OR)_3 + 2AlCl_3 = SiO_3Al_2Cl_4 + 3RCl}.$$

If we write the formula of the product



$$\mathrm{SiO}{<}\begin{array}{l}\mathrm{OAlCl_2}\\ \mathrm{OAlCl_2}\end{array},$$

it appears that in this form also the aluminium might be fixed, but that if more chloride be present, leading to the formation of

$$\mathrm{SiCl(OAlCl_2)_3},$$

such a body would, by virtue of the silicon chlorine present, decompose at once into $\mathrm{AlCl_3}$ and $\mathrm{SiO(OAlCl_2)_2}$. Two atoms aluminium are therefore the most that can possibly be held by one atom silicon reacting as monochlorsilicate; any further amount must remain finally as unchanged chloride. The stability of such bodies as $\mathrm{SiO(OAlCl_2)_2}$ is, however, made improbable by the experiments, which show that even with the ratio 1 : 1 only a part of the aluminium remains fixed.

These equations do not explain the semi-catalytic action of aluminium chloride in decomposing indefinitely large amounts of monochlorsilicate. The reason is obvious when we consider that, as the experiments show, the greatest amount of aluminium which can be held fixed by 1 mol. wt. monochlorsilicate, lies between ⅔ and 1 at. wt. (equations *b* and *d*). Any greater amount of monochlorsilicate will, by virtue of its silicon chlorine, regenerate aluminium chloride, and be destroyed thereby, until the above proportion is reached. At this point further reaction results only in the sense of *b* and *d*, the regeneration of the chloride ceases, and all aluminium remains fixed.

It will be observed that in these reactions the chlorine going to form ethyl chloride comes proximately from the aluminium chloride, but ultimately, in part, from the chlorsilicate, and that the equations

$$SiCl_3(OR) = SiOCl_2 + RCl,$$
$$SiCl(OR)_3 = SiO_2 + RCl + R_2O$$

are not strictly true, the aluminium acting as the agent by which Cl is transferred from Si to R. The hypothesis might perhaps be further tested by substituting aluminium bromide for the chloride. If the decomposition is due to *influence* only, $SiCl_3(OR)$ should give $SiOCl_2$, and RCl and $AlBr_3$ only, but on the above hypothesis $SiO.Cl_2$ with either RBr and $AlCl_3$ only, or a mixture of RCl, RBr, $AlCl_3$ and aluminium chlorobromides, according to the proportions and the nature of the intermediate products. As this would involve previously studying the question whether a *direct* interchange of chlorine and bromine might occur, the experiment was postponed.

Ethyl dichlorsilicate, $SiCl_2(OR)_2$, from similar considerations, should decompose thus—

$$SiCl_2(OR)_2 = SiO_2 + 2RCl,$$

and it is not possible to devise any probable reaction by which aluminium should remain permanently combined. Therefore the apparent catalytic action should be as obvious here as in the case of the trichlorsilicate. The experiments were, however, defective, probably owing to impure material, and no satisfactory conclusion could be drawn from them.

Ethyl orthosilicate, $Si(OR)_4$.—This body shows a radically different behavior from that of the chlorsilicates, the decomposition being strictly proportional to the relative amount of aluminium chloride used, and in this lies the explanation of the whole series of observations.

We may consider the following cases:

$$Si:Al \begin{cases} < 3:4 & (1) \\ = 3:4 & (2) \\ > 3:4 & (3) \end{cases}$$

the ratio 3:4 being that in which the aluminium chloride contains just enough chlorine to convert all ethyl into ethyl chloride.

(*a*) $3Si(OR)_4 + 4AlCl_3 = Si_3O_{12}Al_4 + 12RCl.$

From considerations mentioned while speaking of the monochlorsilicate, it is obvious that this proportion may result in a certain amount of chlorine remaining combined with the aluminium, up to the limit—

(*b*) $3Si(OR)_4 + 4AlCl_3 = Si_3O_{10}Al_4Cl_4 + 8RCl + 2R_2O.$

For practical reasons given below, the substances could not be made to react in this proportion, the result being a formation of ethyl ether, ethyl chloride, and sublimation of some unchanged aluminium chloride. For the same reason a reaction in the sense of case (1) was practically not to be brought about.

If the reaction were in any sense catalytic, it would follow that by reducing the aluminium chloride below the proportion Si : Al = 3 : 4, the decomposition would still be complete, but the amount of ethyl ether would increase relatively, while that of ethyl chloride would decrease, the limit being, with a trace of aluminium chloride—

$$Si(OR)_4 = SiO_2 + 2R_2O.$$

The actual result was that while with Si : Al = 3 : 1 the decomposition was complete, and approximately in the sense

(*c*) $6Si(OR)_4 + 2AlCl_3 = (SiO_2)_6(Al_2O_3) + 6RCl + 9R_2O,$

the slightest diminution of the amount of chloride below this ratio was followed by some of the silicate remaining totally unchanged. With Si : Al = 3 : 0.9 for instance, it was possible to recover some of it, and with Si : Al = 150 : 1 the merest trace of decomposition was discernible. This proportion in the case of the monochlorsilicate resulted easily in total decomposition. The only possible explanation of this difference is that in the case of the chlorsilicates the apparent contact action is due to constant regeneration of aluminium chloride by silicon chlorine. The tetraethyl ether contains no silicon chlorine, aluminium chloride is not regenerated, and therefore acts only in proportion to the amount originally taken.

An experiment was made which shows the peculiar stability of silicon tetrachloride as compared with the chlorsilicates. It was supposed that since

$$SiCl_3(OR) + \text{trace } AlCl_3 = SiO.Cl_2 + RCl + \text{trace } AlCl_3,$$

by adding to tetraethyl silicate some silicon tetrachloride in the proportion required by the equation

$$Si(OR)_4 + 3SiCl_4 = 4SiCl_3(OR),$$

the chlorine of the tetrachloride would regenerate aluminium chloride, with the final result that solid silicon oxychloride and ethyl chloride would be formed. With even Si : Al = 5 : 1 and in sealed tubes at 100° no solid was formed. Only after heating at 170°, at which temperature the tetrachloride acts on the ether, did total decomposition occur.

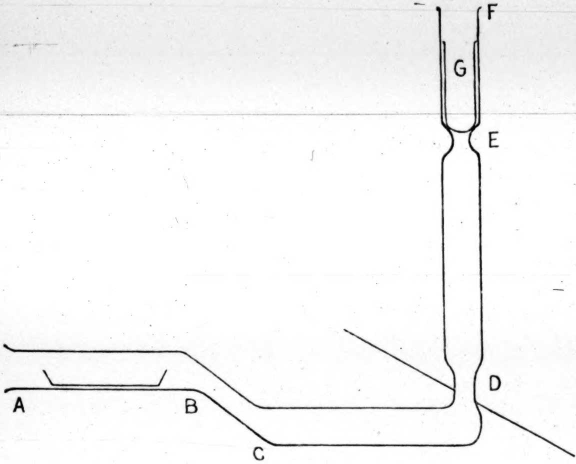
Anhydrous ferric chloride acts on both the tetraethyl silicate and the trichlorsilicate, but with much greater difficulty than aluminium chloride. Only at near the boiling-point (105°) of the trichlorsilicate was any marked reaction, with formation of ethyl chloride, visible. The tetraethyl silicate reacted easily on heating, giving off ethyl ether and ethyl chloride and leaving a solid residue. The reactions were not further studied.

Anhydrous zinc chloride is without action on the tetraethyl silicate at its boiling-point (165°).

EXPERIMENTAL DETAILS.

Only carefully fractioned silicates and freshly sublimed aluminium choride were used. The apparatus and method of working were as follows:

A thin-walled glass tube of about 2 cm. diameter was drawn out into the shape shown in the figure. The constriction *E* served when necessary as a support for the small weighed test-tube *G*, in which the ethyl ether collected. Some aluminium chloride was placed in a boat, inserted into *AB*, and carefully sublimed over into *CD* in a current of dry hydrogen. In this way it was obtained in a finely divided state, rendering solution more rapid. The hydrogen was then replaced by air, *B C* drawn out and melted off at *B*, and the weight of the sublimed chloride determined to a centigram. *CD* was then placed in ice, the calculated weight of silicate or chlorsilicate introduced through *F*, the tube *G* inserted when necessary, and the apparatus attached to an inverted con-



denser which ended in a U-tube with two cocks, placed in a freezing mixture, and serving to condense the ethyl chloride and any ethyl ether that might be carried over. By gently agitating the tube, the solution of the chloride was effected. On removing from the ice, the reaction usually began of itself, and often had to be moderated by cooling. After the evolution of ethyl chloride had slackened, *CD* was gently heated, the ethyl ether then distilling and collecting in *G*. After the collection of ether had ceased, *G* was gently warmed, whereby practically all ethyl chloride was driven over, the ether condensing and running back. After removing *G*, the point *B* was broken off and the residue heated in a current of hydrogen until no further effect was observed, any aluminium chloride condensing in *DE*, or sometimes in part being carried over into the condenser. The hydrogen was then displaced, *DF* melted off at *D*, when necessary, and all products determined by weighing. Some of the liquid in the U-tube was brought into a graduated tube over mercury, and any ethyl ether determined by absorption with a drop or two of strong sulphuric acid, the residue being ethyl chloride.

Ethyl Trichlorsilicate.

Taken $SiCl_3(OR)$ 7.66 grams (3 mol. wts.) and $AlCl_3$ 1.91 grams (1 mol. wt.).

On removing the ice from *CD*, the evolution of ethyl chloride began almost at once, and the liquid grew so warm that cooling had to be resorted to to prevent the contents from boiling over. Presently a large quantity of a colorless, apparently crystalline substance separated, nearly filling the liquid. Its nature was not determined, but it was found to fuse on gently heating. After the evolution of ethyl chloride had moderated, its formation was promoted by a gentle heat. The liquid then became gradually thick, and finally almost solid. *B* was then broken off, and the residue heated in a stream of hydrogen until no further sublimation of aluminium chloride was observed. Absolutely no ethyl ether was formed. The residue was somewhat discolored, solid, transparent and frothy. As explained above, the reaction occurs in accordance with the equation

$$SiCl_3(OR) + xAlCl_3 = SiO\,Cl_2 + RCl + xAlCl_3,$$

as is borne out by the following data, which in this as in all following experiments, are given in percentage of the total material used.

	Found.	Calculated.
Residue	46.3	51.2
Sublimate, ($AlCl_3$)	20.9	19.9
Distillate, RCl	22.5	28.8

The results are naturally only approximate, but quite as near as could be expected. The viscosity of the liquid towards the end interferes with the smoothness of the reaction, and it is impossible to condense the ethyl chloride completely, or to prevent some being carried off by the current of hydrogen. If the reactions given are correct, the residue is not really $SiO.Cl_2$, but a mixture of oxychlorides in which there remains a small amount of ethyl, which will not go off at a temperature below that at which carbonisation and other secondary changes take place, and which are still greater in the cases below mentioned. Troost and Hautefeuille[1] have shown that the result of heating oxychlorides is an approximation towards SiO_2 and $SiCl_4$. This is doubtless the reason why in this case the weight of the residue is slightly too low, and that of the sublimed aluminium chloride a little too high. The former, on extracting with alcohol, left a little silica in gelatinous form, while the latter was found to contain a small amount of volatile silicon compounds. In fact, the residue, on heating in a test-tube to redness, gave off a considerable amount of volatile oxychlorides, but no aluminium chloride.

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[1] Loc. cit.

In experiment 2, the proportions taken were the same and the observations essentially similar.

	Found.	Calculated.
Residue	38.9	51.4
$AlCl_3$ (sublimed)	21.2	19.8
RCl	22.4	28.8

The residue consisted mostly of oxychlorides, soluble in alcohol, and considerable silica (insoluble in alcohol). A portion of the same residue gave—

	Found.	Calc. for $SiO.Cl_2$.
Si	27.08	24.35

The excess of silicon is due as before to a partial volatilisation of oxychlorides with a low percentage of silicon. This residue also contained a very small amount of aluminium, which was completely extracted by alcohol, and therefore present as chloride, not as silicate or oxide. No ethyl ether was formed.

In experiment 3, the residual aluminium was determined in the residue, after heating to dull redness in hydrogen. The amount found, calculated as chloride, was only 3.5 per cent. of the total chloride used. A small amount was to be expected, as it is practically impossible to expel it completely from the solid frothy residue. The conclusion that the chloride remains unchanged at the end of the reaction may therefore be accepted without hesitation.

Ethyl Dichlorsilicate.

This calls for the reaction

$$SiCl_2(OR)_2 + xAlCl_3 = SiO_2 + 2RCl + xAlCl_3.$$

Two experiments were made, one with Si : Al = 50 : 1, the second with Si : Al = 3 : 1. In both cases the decomposition was readily brought about; in the first almost as easily as in the second, but only in the second could any aluminium chloride be recovered, and then not the whole amount used. A small amount of ethyl ether was also formed in each case. As there were reasons for suspecting the sample to contain monochlorsilicate (which would explain the discrepancy), and as no more was available, the quantitative data are omitted.

Ethyl Monochlorsilicate.

Four experiments were made in which the following proportions were observed:

$$Si:Al = \begin{cases} 3:3 & (1) \\ 3:2 & (2) \\ 3:1 & (3) \\ 150:1 & (4) \end{cases}$$

For case (1) the following equations hold, according as the chlorine of the aluminium chloride is completely given off as ethyl chloride, or as it remains in part as $\substack{O \\ O}\!>AlCl$.

$$(a) \qquad 3SiCl(OR)_3 + 3AlCl_3 = Si_3Al_2O_9 + 9RCl + AlCl_3.$$

$$(b) \qquad 3SiCl(OR)_3 + 3AlCl_3 = 3(SiO_3AlCl) + 9RCl.$$

Taken, 6.21 grams $SiCl(OR)_3$ and 4.19 grams $AlCl_3$, or equal mol. wts.

The course of the reaction was essentially the same as with the trichlorsilicate, except that no solid was deposited. The liquid became gradually thicker, with evolution of ethyl chloride, and then quite suddenly stiff at about 75°. On heating in a current of hydrogen, a considerable volume of uncondensible hydrocarbon gas was given off, whereby some aluminium chloride was carried into the condenser and receiver. This was collected and determined. The amount of aluminium fixed in the residue was also determined. No ether collected, and none could be found by absorption over sulphuric acid.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	37.5	28.4	45.9
Al in residue	7.3	5.4	8.1
$AlCl_3$ (sublimed)	3.5	13.5	...
R_2O	...	...	...

The reaction occurs, therefore, in a form combining (*a*) and (*b*), the residue probably consisting in part of aluminium silicates, in part of chloraluminium silicates.

For case (2) where Si : Al = 3 : 2, there are also two ultimate equations possible:

$$(a) \qquad 3SiCl(OR)_3 + 2AlCl_3 = Si_3O_9Al_2 + 9RCl.$$
$$(b) \qquad 3SiCl(OR)_3 + 2AlCl_3 = Si_3O_8Al_2Cl_2 + 7RCl + R_2O.$$

Taken, $SiCl(OR)_3$, 12.93 grams; $AlCl_3$, 5.80 grams; or exactly 3 : 2 mol. wts. The reaction was essentially similar to that in the last experiment, and took place quite as readily as when more chloride was used. The same gradual thickening and sudden stiffening of the liquid were noticed. On finally heating to dull redness in hydrogen, gas was evolved, and a somewhat carbonaceous black vitreous residue was left, but no aluminium chloride sublimed. A small amount of ethyl ether was formed, which was determined by absorption.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	36.0	32.7	39.1
Al in residue	6.1	6.2	6.2
$AlCl_3$ (sublimed)	...	...	...
R_2O	2.5	...	8.6
RCl	33.5	67.3	52.3

Here, too, the reaction is intermediate between (*a*) and (*b*), some R_2O is formed, but all aluminium remains in the residue.

Case (3), where Si : Al = 3 : 1, also admits of two equations:

$$(a) \qquad 6SiCl(OR)_3 + 2AlCl_3 = Si_6Al_2O_{15} + 12RCl + 3R_2O.$$
$$(b) \qquad 6SiCl(OR)_3 + 2AlCl_3 = Si_6Al_2O_{14}Cl_2 + 10RCl + 4R_2O.$$

Taken, $SiCl(OR)_3$, 14.72 grams; $AlCl_3$, 3.30 grams, or 3 : 1 mol. wt. The same thickening, and sudden stiffening at 75° were observed. The reaction began at the same low temperature, and was nearly as rapid as with more chloride. Ethyl ether collected in the tube *G* in abundance, and was identified by its boiling at 30°–35°. The solid residue was nearly colorless, and only on high heating did discoloration ensue. No chloride sublimed. The ether was determined by weighing that collected, and absorbing the small amount found in the distillate as before.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	43.1	31.7	38.4
$AlCl_3$ (sublimed)	...	...	...
R_2O	20.0	15.2	22.0

Although the residue was somewhat too large, the amount of ether showed that the reaction was mainly in the sense of (*b*).

Case (4). In this experiment, 1 mol. wt. aluminium chloride was made to act on 150 mol. wts. monochlorsilicate, or almost a mere trace of the former (taken, 13.38 grams silicate to 0.06 gram chloride). The facts noted were the same as in the other experiments, including the sudden solidifying of the residue. The only difference was that the reaction took place rather more slowly, owing to the small amount of chloride present, and that the residue left at red heat was of purplish color, showing very little carbonisation. The ease with which the decomposition took place indicated that a much smaller amount of aluminium chloride would have been sufficient. The ethyl ether showed the correct boiling-point.

The equation for a trace of aluminium chloride is practically

$$SiCl(OR)_3 = SiO_2 + RCl + R_2O\,.$$

The actual results were:

	Found.	Calculated for Si : Al = 150 : 1.
Residue	30.8	30.3
R_2O	32.7	36.8
RCl	11.2	33.0

The amount of ether was 89 per cent. of the theoretical.

Tetraethyl Silicate.

Four experiments may be mentioned, into which the following proportions entered:

$$Si:Al = \begin{cases} 3:4 & (1) \\ 3:1 & (2) \\ 3:0.9 & (3) \\ 150:1 & (4) \end{cases}$$

The hypothetical equations for (1) and (2) are given under the general considerations on the decomposition of the tetraethyl silicate (*a*, *b* and *c*).

For experiment (1) were taken 5.95 grams $Si(OR)_4$, 5.09 grams $AlCl_3$, or 3 : 4 mol. wts. It was not possible to cause the chloride to dissolve completely in this amount of ether, and the result was a mixture of varying composition, from which no definite result could be expected. The general course of the reaction was the same as in other cases. Some ethyl ether was formed, but a little aluminium chloride also sublimed, indicating an excess in one part of the mass and a deficiency in another.

In experiment (2) with Si : Al = 3 : 1 the mixture evolved ether and ethyl chloride, and finally became solid, and on further heating gave off gases, but no aluminium chloride. Only about one-half the theoretical amount of ether was obtained, the remainder appearing as hydrocarbon gas and empyreumatic substances.

In experiment (3) with Si : Al = 3 : 0.9 it was noticed that some unchanged silicate distilled at the end of the operation. It appears, therefore, that the least amount of aluminium chloride required to effect total decomposition is 1 mol. wt. to 3 mol. wts. of the silicate. This is strikingly seen in the next experiment (4), which at the same time shows the radical difference in their behavior towards aluminium chloride of the silicates and chlorsilicates.

Taken, 16.37 grams $Si(OR)_4$, 0.07 $AlCl_3$, or 150 : 1 mol. wts. Even on boiling strongly for an hour at about 165°, no marked reaction was noticed. The liquid remained clear and limpid, and not over 0.1 gram ethyl ether collected. At the end of an hour the silicic ether was distilled off unchanged, leaving but a trace of solid residue. It was therefore clear that only a trace had been decomposed, corresponding to the trace of chloride used.

The decomposition of monochlorsilicates by a trace of aluminium chloride might perhaps be utilised to obtain other ethers than ethyl ether. It is known that the continuous process for obtaining ethyl ether from alcohol by means of sulphuric acid does not apply to the alcohols above propyl alcohol.[1] Isobutyl alcohol, for instance, does not give a trace of isobutyl ether. The silicates of the monatomic aliphatic alcohols, as far as has been investigated, are easily prepared, and of all the chlorsilicates, the monochlorsilicates are the most easily made. By adding to 1 mol. wt. silicon tetrachloride 3 mol. wts. of the alcohol, boiling the product or heating to 170° under pressure, and finally distilling with a trace of aluminium chloride, a product should be obtained, consisting of a mixture of ether and chloride, which could be easily separated. From ethyl monochlorsilicate 89 per cent. of the theoretical yield of ethyl ether was thus obtained.

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[1] Norton and Prescott, This Journal **6**, 241.

On the Isolation of the Intermediate Products.

Aluminium chloride is insoluble in carbon bisulphide; if, however, a mixture of about 1 vol. tetraethyl silicate and 4 vols. carbon bisulphide be boiled with some aluminium chloride, the latter liquefies and partly dissolves, while there is an evolution of permanent gas, presumably ethyl chloride. On decanting the warm liquid a considerable amount of oil separates. This oil is not volatile, and on heating gives a solid residue resembling that obtained by the direct action of the chloride on the silicic ether. The carbon bisulphide solution, if concentrated out of contact with moisture, deposits on cooling a mass of well-formed rectangular crystals, or on evaporation *in vacuo* over paraffine shavings leaves a perfectly dry crystalline mass. A portion of such a bisulphide solution was decomposed by ammonia and the ratio of Si : Al : Cl determined. It was found to be 1 : 2.1 : 3.9, or very nearly 1 : 2 : 4, a result which may, of course, have been accidental. The oil which separates is soluble in a fresh portion of hot carbon bisulphide, but it appears readily to change, for a greater amount is required than that from which it separated, and by boiling out with small quantities of bisulphide, a residue is left which is finally almost solid. These facts seem to indicate the possibility of isolating some of the intermediate products, but this has not yet been attempted.

In conclusion, I wish to express my thanks to the Director of the Geological Survey, and to Prof. F. W. Clarke, for the means and opportunity of carrying out these experiments.

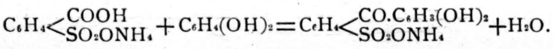
U. S. GEOLOGICAL SURVEY, WASHINGTON, *August* 1, 1892.

INVESTIGATIONS ON THE SULPHON-PHTHALEÏNS.

II.—DIOXYBENZOYL-BENZENE-SULPHONIC ACID AND SULPHON-FLUORESCEÏN.[1]

BY CHARLES C. BLACKSHEAR.

Remsen and Linn have shown[2] that the chief product of the action of resorcin on the acid ammonium salt of ortho-sulphobenzoic acid is the ammonium salt of dioxybenzoyl-benzene-sulphonic acid, the reaction being represented thus:



$$C_6H_4<\begin{matrix}COOH\\SO_2ONH_4\end{matrix} + C_6H_4(OH)_2 = C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_2ONH_4\end{matrix} + H_2O.$$

From the ammonium salt they prepared the free acid and from this the barium salt, and they analysed these three substances, but the acid and its derivatives were not further studied by them. At the suggestion of Professor Remsen I took up this study and the results obtained by me are recorded in this article.

Preparation of Dioxybenzoyl-benzene-sulphonic Acid.

The starting-point in the preparation of this compound was the benzoic sulphinide contained (to the extent of about 50 per cent.) in commercial saccharin. This was treated according to the method described by Remsen and Burton[3] as follows:

In a flask connected with an inverted condenser fifty grams saccharin were boiled with hydrochloric acid of such strength that thirteen parts contained one part concentrated hydrochloric acid. Within half to three-quarters of an hour all the saccharin passed into solution, and after boiling for three hours the desired transformation was complete—the solution had completely lost its sweet taste. Parasulphamine-benzoic acid crystallised from the solution on cooling. After the contents of the flask had thoroughly cooled the solution was filtered and the filtrate evaporated to dryness on the water-bath. On adding a little cold water to the residue very nearly all dissolved, and the acid ammonium salt crystallised from the filtered solution after evaporation to a very small volume. The method is very quick and effective.

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[1] From the Author's Thesis for the degree of Doctor of Philosophy, Johns Hopkins University, June, 1890.

[2] This Journal **11**, 73.

[3] This Journal **11**, 403.

The acid ammonium salt of ortho-sulphobenzoic acid being prepared, the next step is its conversion into the ammonium salt of dioxybenzoyl-benzene-sulphonic acid. This was effected by the action of resorcin in the following manner: Fifteen grams of the salt and twelve grams resorcin were placed in a small beaker which was heated gradually in a sulphuric-acid bath. A thermometer, suspended from above, was in contact with the mixture in the beaker. The resorcin melted first, and as the temperature rose the acid ammonium salt began to melt. At a temperature between 170° and 175°, and before all the acid ammonium salt had melted, the mixture was stirred with the thermometer and very soon the reaction began. The stirring was continued until the reaction became quite vigorous, and as soon as the rapidity of the reaction began to diminish it was recommenced and kept up almost continuously thereafter. After about an hour the acid ammonium salt had all melted and there was no further evolution of water. Very soon afterwards the yellow, silky crystals of the ammonium salt began to make their appearance in the dark red liquid. Crystallisation proceeded tolerably rapidly, and in the course of half an hour or so the mass was almost solid, even at this high temperature (175°–180°). The beaker was then removed from the bath and the product of the reaction was dissolved in hot water. The solution (which was reddish yellow and somewhat fluorescent) was evaporated to a small volume. On cooling, the ammonium salt separated in small yellow crystal plates arranged in aggregates. These were subsequently recrystallised after treatment with animal charcoal. With a small portion of the salt this operation was repeated several times, and finally some very nearly colorless crystals were obtained. The reaction between the acid ammonium salt of ortho-sulphobenzoic acid and resorcin takes place best at a temperature of about 180°, and the operation requires, from beginning to end, not more than two and a half to three hours. The stirring seems necessary, since in one experiment in which stirring was omitted the crystals of the ammonium salt were not formed, even though the mixture was heated at 178°–185° for nearly two days. On subsequently stirring this same mixture the reaction took place readily at 180°.

The preparation of dioxybenzoyl-benzene-sulphonic acid from its ammonium salt was effected in the following manner: To a concentrated solution in a large Erlenmeyer flask a small quantity of finely pulverised litharge was added. The solution was boiled on a sand-bath, the flask being connected with an inverted condenser. The ammonium salt is thus gradually converted into a basic lead salt, which separates as an insoluble precipitate. This basic salt was filtered off from time to time (separation from the heavier lead oxide that remained being effected by decantation), the solution evaporated to a small volume, and again boiled with lead oxide. By this method (using four large Erlenmeyer flasks and starting with a little more than fifty grams of the ammonium salt in each flask) about 210 grams of the salt were converted into basic lead salt in two to three days. During the process of boiling, crystals of ammonium carbonate appeared in the condenser tube, due evidently to slight decomposition. The solution of the ammonium salt must be concentrated, otherwise the transformation is exceedingly slow. The basic lead salt is insoluble or extremely difficultly soluble in water, but can easily be dissolved if boiled with a small quantity of water to which some acetic acid is added. The solution in acetic acid when sufficiently concentrated deposits, on cooling, crystals of moderate size. These crystals, on standing in the air, soon become opaque and pulverulent, owing, doubtless, to loss of their water of crystallisation. Analyses of these crystals gave the following results:

I. 0.26943 gram of the salt, heated two to three hours at 150°–160°, lost 0.03024 gram H_2O. Percentage H_2O, 11.22.

II. 0.25082 gram of the salt, heated two to three hours at 150°–160°, lost 0.02823 gram H_2O. Percentage H_2O, 11.26.

III. 0.29044 gram of the salt gave 0.13799 gram $PbSO_4$. Percentage Pb in crystallised salt, 32.43.

IV. 0.21651 gram of the salt gave 0.1028 gram $PbSO_4$. Percentage Pb in crystallised salt, 32.41.

V. 0.2701 gram of the salt gave 0.12892 gram $PbSO_4$. Percentage Pb in crystallised salt, 32.58.

No single formula which is plausible, and at the same time satisfies the above conditions as to percentage of lead and water, suggests itself, and the most natural inference is that the substance was a mixture of two or more basic salts of lead.

Dioxybenzoyl-benzene-sulphonic acid can be prepared from the acetic acid solution of the basic lead salt by precipitation of the lead by hydrogen sulphide. Since the acid is extremely easily soluble in both hot and cold water, it was necessary to evaporate its solution to a very small volume in order to obtain it in crystallised condition.

By adding much cold water to a very small quantity of the finely powdered, crystallised basic lead salt, solution can be effected without the addition of acetic acid, though if the solution be allowed to stand for a few minutes the basic salt will begin to separate. Now from the clear solution, from which the lead was immediately precipitated by hydrogen sulphide, colorless crystals of dioxybenzoyl-benzene-sulphonic acid were obtained. Nearly all the acid used for these investigations was prepared by the first method, that is, by precipitation of the lead from the acetic acid solution of the basic salt not previously crystallised. The crystals of the acid, as thus obtained, were always more or less dark, though by subsequent treatment with animal charcoal this color was very nearly all removed.

The acid crystallises in plates, apparently monoclinic, some of the crystals measuring as much as two to three millimeters in length and breadth.[1] When a solution of the acid is evaporated on the water-bath a yellow color is noticed on the sides of the dish near the surface of the solution, and a pink color is observable in the same parts as the solution becomes more concentrated. This is evidently due to decomposition, the acid tending, even at this temperature, to change to sulphon-fluoresceïn. The acid is soluble in alcohol, but is insoluble or only slightly soluble in ether.

Starting with 500 grams saccharin, containing about 250 grams benzoic sulphinide, the yield of dioxybenzoyl-benzene-sulphonic acid was 140 grams.

I. 0.3198 gram substance gave 0.5269 gram CO_2 and 0.1468 gram H_2O.[2] (This combustion was made by Mr. R. J. J. De Roode, Jr.)

II. 0.39665 gram substance gave 0.64221 gram CO_2 and 0.16283 gram H_2O.

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[1] The faces of the crystals were so imperfect that accurate crystallographic measurements could not be obtained.

[2] The method of combustion employed in the analyses of this acid and of sulphon-fluoresceïn was that recommended by De Roode, This Journal **12**, 226.

III. 0.38127 gram substance gave 0.61856 gram CO_2 and 0.16173 gram H_2O.

IV. 0.19193 gram substance gave 0.13045 gram $BaSO_4$ (Pearson's method).

V. 0.18916 gram substance gave 0.1263 gram $BaSO_4$ (Pearson's method).

	Calculated for $C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_2OH\end{matrix}+3H_2O.$	Found. I.	II.	III.	IV.	V.
C	44.83	44.93	44.16	44.25	...	...
H	4.60	5.10	4.56	4.71	...	...
S	9.20	...	...	...	9.33	9.17

The composition of the crystallised acid as given by Remsen and Linn on the basis of sulphur estimations alone was $C_{13}H_{10}O_6S + 2H_2O$, but the above results are not reconcilable with this and indicate unmistakably a composition represented by $C_{13}H_{10}O_6S + 3H_2O$. No attempt was made to estimate the water of crystallisation, since Remsen and Linn found such an estimation impossible, on account of the tendency of the acid to change to sulphon-fluoresceïn under the influence of heat.

Barium salt, $\left(C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2Ba+6H_2O$.—This salt (previously prepared and described by Remsen and Linn[1]) was prepared by treating a hot solution of the acid with pure barium carbonate. It crystallises in small plates which are nearly colorless. Analyses gave the following results:

I. 0.29577 gram of the salt, heated for several hours at 170°–180°, lost 0.03787 gram H_2O.

II. 0.22316 gram of the salt gave 0.06221 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2Ba+6H_2O.$	Found. I.	II.
H_2O	13.00	12.80	...
Ba	16.49	...	16.39

Calcium salt, $\left(C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2Ca+4H_2O$.—The calcium salt was prepared by treating a hot solution of the acid with finely pulverised calcite. It is very easily soluble, even in cold water, but on evaporation to a small volume very small, thin crystals were deposited which were colorless and arranged in radial groups. The analyses resulted as follows:

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[1] Loc. cit.

I. 0.05384 gram of the salt, heated for one hour at 140°–145°, lost 0.00562 gram H_2O.

II. 0.0936 gram of the salt, heated for one hour at 140°–145°, lost 0.0099 gram H_2O.

III. 0.19723 gram of the salt gave 0.039 gram $CaSO_4$.

IV. 0.1005 gram of the salt gave 0.01977 gram $CaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\SO_3\end{smallmatrix}\right)_2Ca + 4H_2O$.	Found. I.	II.	III.	IV.
H_2O	10.32	10.44	10.58	...	...
Ca	5.73	...	...	5.82	5.79

Lead salt, $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\SO_3\end{smallmatrix}\right)_2Pb + 7H_2O$.—A hot solution of the acid was treated with lead carbonate in expectation of preparing a basic salt similar to the substance obtained by boiling the ammonium salt with litharge. The salt actually obtained, however, was not a basic salt but the normal salt. It is readily soluble in hot water; not very easily soluble in cold water. When its solution was evaporated on the water-bath it exhibited no tendency to change to a basic salt. The salt crystallised well, the crystals being small and apparently rhombohedral. On one occasion it was obtained in the form of long, thin crystals, but on dilution of the mother-liquor and stirring, these soon changed to the small rhombohedra. Analysis gave the following figures:

I. 0.19415 gram of the salt, heated for three hours at 145°–155°, lost 0.02642 gram H_2O.

II. 0.21537 gram of the salt, heated for three hours at 145°–155°, lost 0.02944 gram H_2O.

III. 0.19651 gram of the salt gave 0.06378 gram $PbSO_4$.

IV. 0.20673 gram of the salt gave 0.06689 gram $PbSO_4$.

V. 0.20059 gram of the salt gave 0.06492 gram $PbSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}CO.C_6H_3(OH)_2\\SO_3\end{smallmatrix}\right)_2Pb + 7H_2O$.	I.	II.	Found. III.	IV.	V.
H_2O	13.72	13.61	13.67	...	...	...
Pb	22.48	...	...	22.15	22.09	22.09

Silver salt, $C_6H_4<\begin{smallmatrix}CO.C_6H_5(OH)_2\\SO_2OAg\end{smallmatrix} + 2H_2O$.—The silver salt was prepared by treating a warm solution of the acid with pure, freshly precipitated silver carbonate. Much care was necessary in the preparation and crystallisation of the salt. The solution readily assumed a dark color. Heating seemed to facilitate this, and on evaporation of the solution on the water-bath a small quantity of a black powder separated. The salt is readily soluble in hot water and moderately soluble in cold water; it crystallises in colorless, lath-shaped crystals, radially arranged. The analyses gave the following results:

I. 0.013819 gram of the salt heated for about three hours at 100°–110°, lost 0.01162 gram H_2O.

II. 0.14157 gram of the salt, heated for about three hours at 100°–110°, lost 0.01218 gram H_2O.

III. 0.21318 gram of the salt gave 0.07556 gram Ag_2SO_4.

IV. 0.22971 gram of the salt gave 0.07395 gram AgCl.

	Calculated for $C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_2OAg\end{matrix}+2H_2O$.	Found.			
		I.	II.	III.	IV.
H_2O	8.25	8.41	8.60	...	...
Ag	24.63	...	...	24.50	24.20

Copper salt.—This salt was prepared by treatment of a solution of the acid with freshly precipitated basic copper carbonate. Its solution was of a dark green color. Attempts at crystallisation were not attended with much success. In one instance a few extremely small crystals separated, but after standing in the mother-liquor a day or two they had apparently lost their crystalline character.

Attempted Preparation of an Ethereal Salt of Dioxybenzoylbenzene-sulphonic Acid.

In the hope of preparing an ethereal salt of the acid, both the silver and the lead salt were treated with ethyl iodide. The experiments gave negative results and may be described, briefly, as follows:

A small quantity of ethyl iodide and a few crystals of the silver salt were enclosed in a pressure bottle and the ethyl iodide was boiled for an hour or more. The crystals became opaque, but this, apparently, was the only change that took place. After filtration the filtrate was evaporated and a glutinous mass remained. This was dissolved in acetic anhydride and the solution evaporated until the odor of acetic acid had disappeared. A glutinous mass was again left. Water was added and the solution filtered from a very small quantity of solid matter. The filtrate was treated with barium carbonate. After filtration and concentration of the solution a few crystals separated. There was not enough of them for a careful examination, but tests for acetic acid showed that they were not crystals of barium acetate.

An experiment with the normal lead salt was performed in the same manner as that just mentioned, but the lead salt, in this case, was not in the least affected by ethyl iodide. Subsequently, this experiment was modified by dissolving a small quantity of the lead salt in alcohol, then adding ethyl iodide and boiling in a pressure bottle. In this case a little lead iodide separated. The solution was filtered from this, the filtrate evaporated, treated with acetic anhydride and, subsequently, with barium carbonate—exactly in the manner described in the experiment with the silver salt. The result was practically the same as with the silver salt. No crystals separated, however, after treatment with barium carbonate. On evaporation to dryness there was only a slight residue.

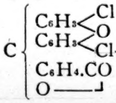
Action of Acetic Anhydride on Dioxybenzoyl-benzene-sulphonic Acid.

Several attempts were made to prepare an acetyl derivative of this acid. The experiments were conducted as follows:

Two grams dioxybenzoyl-benzene-sulphonic acid and three grams acetic anhydride being enclosed in a sealed tube, the tube was placed in a water-bath and heated to the temperature of boiling water. The acid easily dissolved in the acetic anhydride. The solution, which was of a light yellow color at first, gradually changed to red, and when, after the expiration of about three hours, the heating was discontinued it was quite red and exhibited distinct fluorescence. The solution was evaporated on the water-bath (water being added from time to time) until the odor of acetic acid could no longer be detected. It was then boiled with pure barium carbonate in order to prepare a barium salt of the substance in solution. The salt thus prepared crystallised on cooling its moderately concentrated solution, and the crystals obtained closely resembled those of the barium salt of the original dioxybenzoyl-benzene-sulphonic acid. Analyses showed that the substance actually was this salt. It is therefore clear that an acetyl derivative of this acid cannot be prepared by heating it with acetic anhydride in a sealed tube at 100°. The change in color of the solution and the fluorescence observed were probably due to the formation of a very small quantity of sulphon-fluoresceïn under the influence of heat.

Experiments with acetic anhydride at 150° and even at 170° gave no better results.

Action of Phosphorus Pentachloride on Dioxybenzoyl-benzene-sulphonic Acid.

By the action of phosphorus pentachloride on fluoresceïn Baeyer prepared a dichlor derivative of the same, represented thus:  $C\left\{\begin{array}{l} C_6H_3<^{Cl}_{O} \\ C_6H_3<_{Cl} \\ C_6H_4.CO \\ O\text{———}\lrcorner \end{array}\right.$—two chlorine atoms replacing the two hydroxyl groups.[1] It seemed probable that an analogous derivative of dioxybenzoyl-benzene-sulphonic acid might be prepared—a derivative in which one or both of the hydroxyl groups of the resorcin residue would be replaced by chlorine. In the hope of obtaining such a substance, and in order to study the action of phosphorus pentachloride on the acid, whatever this action might be, the work described below was undertaken.

The first experiment was conducted in the following manner: Two grams of the acid were mixed with eight grams phosphorus pentachloride. Quite a vigorous reaction ensued. When this seemed about at an end the product was heated on a water-bath and was stirred from time to time. The liquid assumed a dark red color and became more viscous. After the expiration of about ten minutes it began to harden rapidly, and was therefore removed from the water-bath. A sample treated with dilute sodium hydroxide solution dissolved with comparative ease. This solution was decidedly fluorescent, exhibiting in transmitted light a pink color, very similar to that of eosin. Another sample was treated with alcohol, in which it dissolved with comparative ease, but no crystals could be obtained from the solution. The remainder of the product of the reaction was treated with cold water. A portion dissolved, leaving a white plastic mass; but this, too, was found to be passing into solution, and on heating dissolved with great ease. The solution was heated on the water-bath until the odor of hydrochloric acid could no longer be detected. The viscous mass remaining was diluted with water and the solution treated with barium carbonate in order to prepare a barium salt of the substance obtained. This salt crystallised well, and analysis of the same gave the following results:

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[1] Ann. Chem. (Liebig) **183**, 18.

I. 0.07937 gram of the salt, heated for an hour at 110°–120°, lost 0.01099 gram H_2O. Percentage H_2O, 13.85.

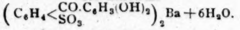
II. 0.1 gram of the salt gave 0.02858 gram $BaSO_4$. Percentage Ba in crystallised salt, 16.80.

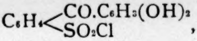
Since no definite conclusion could be deduced from these figures, another portion of the acid was treated with phosphorus pentachloride.

This second experiment was conducted in much the same manner as the foregoing. The product of the reaction between the two substances, when heated on the water-bath, was not stirred as in the former case, and, consequently, the liquid did not become hard, and the red color appeared only where the sides of the dish came in contact with the surface of the solution. The product of the reaction dissolved with comparative ease in water, even when ice was added, though not so readily. The solution was evaporated until the hydrochloric acid was eliminated, and the concentrated solution remaining was allowed to stand over night. By the next morning solid matter, arranged in spherical masses, had separated. This dissolved on addition of water. The solution was boiled with barium carbonate. On evaporation of the filtered solution a crystalline substance soon began to separate. This proved to be barium phosphate, and was filtered off after the solution had been reduced to a very small volume. From the filtrate small, flat crystals of a light yellow color separated. These contained a trace of chlorine, doubtless due to impurity. The results of the analyses show conclusively that the substance was the barium salt of the original dioxybenzoyl-benzene-sulphonic acid.

I. 0.08505 gram of the salt, heated for two and a half hours at 118°–120°, lost 0.01093 gram H_2O.

II. 0.10357 gram of the salt gave 0.02841 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4<^{CO.C_6H_3(OH)_2}_{SO_3}\right)_2Ba+6H_2O$.	Found. I.	Found. II.
H_2O	13.00	12.85	...
Ba	16.49	...	16.13

It seems probable that the action of phosphorus pentachloride, or at least its chief action, led to the formation of the chloride of dioxybenzoyl-benzene-sulphonic acid,  $C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_2Cl\end{matrix}$, and that on treating this latter with water the acid was regenerated. The investigation was continued, since it hardly seemed possible that, under proper conditions, the acid could resist further action of the phosphorus pentachloride.

The third experiment differed but slightly from the two preceding. A little more phosphorus pentachloride was used, the product of the reaction was heated on the water-bath for a longer time, until all hydrochloric acid was eliminated, and was frequently stirred meanwhile. Afterwards the red viscous mass was diluted, treated with barium carbonate and then with animal charcoal. The barium salt obtained (in connection with barium phosphate) closely resembled the barium salt of dioxybenzoyl-benzene-sulphonic acid, and contained only a trace of chlorine. The analyses given below indicate that it actually was this substance. Since the salt was, doubtless, not perfectly free from impurities, the variation from the theoretical percentages is hardly more than might be expected.

I. 0.09591 gram of the salt heated for one and a half hours at 110°–120°, lost 0.01331 gram H_2O.

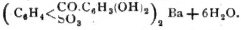
II. 0.10653 gram of the salt gave 0.02889 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2Ba+6H_2O$.	Found. I.	Found. II.
H_2O	13.00	13.88	...
Ba	16.49	...	15.95

On evaporation of the mother-liquor of the barium salt a resinous substance of a light red color separated. This became hard on cooling. A portion of it dissolved in alcohol, and on evaporation separated again, but not in crystalline form. It contained barium and also chlorine. When treated with alkali, a beautiful fluorescence was developed, and the pink color in transmitted light was strikingly like that of eosin. The substance was not of such a nature as to warrant a thorough investigation. The probability is that a portion of it consisted of the remainder of the barium salt of dioxybenzoyl-benzene-sulphonic acid, and that a very small portion, doubtless that to which the red color was due, was a chlorine derivative of sulphon-fluoresceïn, similar to eosin (tetrabrom-fluoresceïn).

The object of the experiment now to be described is the study of the action of phosphorus pentachloride on the acid at a temperature considerably higher than that of the former experiments. Two grams of the acid and somewhat more than eight grams of phosphorus pentachloride were placed in a small retort which was heated in a sulphuric-acid bath. The temperature of the bath rose gradually, and between 135° and 170° phosphorus oxychloride, together with some pentachloride, passed into the receiver. When the temperature of 170° was reached the distillation seemed about at an end, so the heating was discontinued. The product in the retort—somewhat dark in color and hard when cold—was treated with cold water. It did not dissolve to an appreciable extent. On warming it became softer, and on boiling it passed very gradually into solution. After evaporation on the water-bath to remove the hydrochloric acid present, water was added, and the solution was boiled with barium carbonate and subsequently with animal charcoal. The salt obtained (in connection with barium phosphate) separated in light yellow crystals which contained only a trace of chlorine. The analysis indicates that they were crystals of the barium salt of dioxybenzoyl-benzene-sulphonic acid, slightly impure.

0.11545 gram of the salt, heated for three hours at 120°–126°, lost 0.01619 gram H_2O and gave 0.03126 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4<^{CO.C_6H_3(OH)_2}_{SO_3}\right)_2 Ba + 6H_2O.$	Found.
H_2O	13.00	14.02
Ba	16.49	15.92

A portion of this barium salt was carefully treated with sulphuric acid to remove the barium. On evaporation of the filtered solution a substance remained which possessed the characteristic properties of dioxybenzoyl-benzene-sulphonic acid. On evaporation of the mother-liquor of the barium salt resinous matter separated just as in the last experiment. In this case, however, it was not red, and when treated with alkali no fluorescence was observed. It was not investigated further.

As a result of all the above experiments it may be stated that dioxybenzoyl-benzene-sulphonic acid when subjected to the action of phosphorous pentachloride, and heated even as high as 170°, is not by any means entirely transformed into a compound in which either one or both hydroxyl groups of the resorcin residue are replaced by chlorine. If such a product is formed at all it is only to a limited extent, the chief action leading evidently to the formation of the chloride of the acid, from which the free acid is regenerated on treatment with water.

Action of Concentrated Nitric Acid on Dioxybenzoyl-benzene-sulphonic Acid.

A small quantity of dioxybenzoyl-benzene-sulphonic acid was gradually added to hot concentrated nitric acid. Reaction took place at once, accompanied by the evolution of red fumes. On subsequently boiling the acid the process of oxidation continued. After boiling for about ten minutes the red liquid was allowed to cool, when long, delicate crystals were deposited. When the nitric acid was evaporated from the mother-liquor and water added to the residue, a white substance remained undissolved, which proved to be some of the same compound, a portion of which had crystallised from the nitric acid. The melting-point of the crystals deposited by the acid solution was 174° (uncorr.), and a solution of the same in water was of a deep yellow color. These facts led to the belief that the compound was styphnic acid (trinitro-resorcin),[1] and the subsequent preparation and examination of the barium salt confirmed this. This salt was not easily soluble in hot water and very difficultly soluble in cold water. When rapidly heated on platinum foil it first assumed a red color and then exploded violently. It crystallised at first in small, orange-yellow needles. On recrystallisation very small, short, prismatic crystals were first deposited; afterwards, longer tabular crystals. Analysis of the prismatic crystals resulted as follows:

0.082 gram of the salt, heated for one hour at 192°–210°, lost 0.0039 gram H_2O and gave 0.04762 gram $BaSO_4$.

	Calculated for $C_6H(NO_2)_3O_2Ba + H_2O$.	Found.
H_2O	4.52	4.76
Ba	34.42	34.15

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[1] Stenhouse found the melting-point of styphnic acid to be 175.5°. Chem. News **23**, 194.

Analysis of the needles obtained on first crystallisation gave 9.14 per cent. H_2O and 32.33 per cent. Ba. In view of the fact that barium styphnate crystallises differently under different conditions—Salkowski,[1] and Lippmann and Fleissner[2] having obtained $C_6H(NO_2)_3O_2Ba + H_2O$, and Stenhouse,[3] and Griess[4] $C_6H(NO_2)_3O_2Ba + 3H_2O$, while Henriques[5] obtained both—the figures last quoted indicate a mixture of $C_6H(NO_2)_3O_2Ba + H_2O$ and $C_6H(NO_2)_3O_2Ba + 3H_2O$.

After separating the styphnic acid as carefully as possible from the total product obtained in the reaction, the residual water solution was evaporated to a very small volume. On allowing the glutinous residue to stand for several hours it became solid and crystalline, and closely resembled ortho-sulphobenzoic acid. Two salts were prepared, the neutral barium salt and the acid barium salt. Both were colored light yellow from the presence of traces of the styphnate. The neutral salt separated in small crystals from a moderately concentrated solution. Analyses of the same resulted as follows:

I. 0.11321 gram of the salt, heated for one and a half hours at 110°–120°, lost 0.00986 gram H_2O.

II. 0.1037 gram of the salt gave 0.06457 gram $BaSO_4$.

	Calculated for $C_6H_4<{CO_2 \atop SO_3}>Ba + 2H_2O$.	Found.	
		I.	II.
H_2O	9.65	8.71	...
Ba	36.73	...	36.61

The acid barium salt was prepared by dividing a portion of the acid into two equal parts, neutralising one part with barium carbonate and then adding the other. It crystallised in long thin needles, analyses of which gave the figures stated below. Remsen and Fahlberg[6] found that the acid barium salt of ortho-sulphobenzoic acid contained two and a half molecules of water of crystallisation, and Remsen and Dohme[7] found four and a half molecules, but the results obtained show that in this case it crystallised with two molecules.

I. 0.10467 gram of the salt, heated for one hour at 110°–120°, lost 0.00612 gram H_2O and gave 0.0426 gram $BaSO_4$.

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[1] Ber. d. chem. Ges. **8**, 637.

[2] Monatsh. Chem. **6**, 817.

[3] Chem. News **23**, 195.

[4] Ber. d. chem. Ges. **7**, 1224.

[5] Ann. Chem. (Liebig) **215**, 340.

[6] Loc. cit.

[7] This Journal **11**, 336.

II. 0.10136 gram of the salt, heated for one hour at 110°–120°, lost 0.00626 gram H_2O and gave 0.04103 gram $BaSO_4$[1].

	Calculated for $\left(C_6H_4<\substack{COOH\\SO_3}\right)_2Ba+2H_2O$.	Found. I.	Found. II.
H_2O	6.26	5.85	6.18
Ba	23.83	23.93	23.80

The results above stated show conclusively that the action of concentrated nitric acid on dioxybenzoyl-benzene-sulphonic acid leads to the formation of styphnic acid and ortho-sulphobenzoic acid.

Action of Concentrated Sulphuric Acid on Dioxybenzoyl-benzene-sulphonic Acid.

The study of the action of concentrated sulphuric acid on dioxybenzoyl-benzene-sulphonic acid led to interesting results, though the time at my disposal was so short as not to permit a satisfactory examination of all the products of decomposition.

A small quantity of dioxybenzoyl-benzene-sulphonic acid was heated with a large excess of concentrated sulphuric acid in a beaker suspended in a sulphuric-acid bath. The acid soon dissolved, and the yellow color of the solution changed to a dark red as the temperature rose. At about 195°, and after stirring the liquid with the thermometer for a short time, reaction took place accompanied by the separation of dark-colored solid matter. The temperature was soon allowed to fall to 185°, and was kept at 185°–190° during the balance of the operation. The contents of the beaker were stirred at intervals. The reaction seemed to continue, though it was much less vigorous than at first. The amount of solid matter increased, but not to such an extent as to render the mass very stiff. After about two and a half hours the source of heat was removed. When the contents of the beaker had cooled, water was added to the same, and the solution was filtered. The filtrate was first examined. It was strongly fluorescent. An excess of barium carbonate was added, and the solution was subsequently filtered, treated with animal charcoal, and evaporated to a small volume. From this moderately concentrated solution a salt separated, which crystallised in prisms elongated in one direction. After a second treatment with animal charcoal and recrystallisation, the salt was obtained in colorless crystals. The properties of this salt and estimation of barium and water leave no room for doubt that it was the barium salt of ortho-sulphobenzoic acid. The analysis resulted as follows:

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[1] Recrystallised salt was used in this second analysis.

0.11196 gram of the salt, heated for one hour at 180°-190°, lost 0.01039 gram H_2O and gave 0.07009 gram $BaSO_4$.

	Calculated for $C_6H_4<{CO_2 \atop SO_3}>Ba + 2H_2O$.	Found.
H_2O	9.65	9.28
Ba	36.73	36.81

The dark-colored solid matter remaining on the filter was afterwards examined. On treatment with moderately concentrated caustic potash a portion of this dissolved, giving an intensely fluorescent solution. This was heated for a short time, but a considerable portion of the solid matter still remained undissolved. After filtration, hydrochloric acid was added to the fluorescent solution, when a reddish brown substance was precipitated. This substance closely resembles sulphon-fluoresceïn (described by Remsen and Linn,[1] and also in this article), the formation of which under the conditions of this experiment might have been expected; yet the percentages of sulphur and water in sulphon-fluoresceïn—sulphur 8.29 per cent., water 4.66 per cent.—are lower than the figures obtained on analysis of the substance, and no definite conclusion can be drawn without further data. The analyses gave the following results:

I. 0.04112 gram substance, heated for one hour at 125°-132°, lost 0.00215 gram $H_2O = 5.23$ per cent. H_2O.

II. 0.14637 gram substance gave 0.09607 gram $BaSO_4$ (Liebig's method) $= 9.01$ per cent. S.

The third product obtained in this reaction, which was insoluble in caustic potash, was a dark brown powder, almost black. Since it seemed insoluble in alcohol and concentrated hydrochloric acid, it was treated with these reagents, in succession, for the purpose of removing impurities. After the treatment with concentrated hydrochloric acid it was thoroughly washed with water and then dried. Estimations of the sulphur gave the following figures:

I. 0.13402 gram substance gave 0.07647 gram $BaSO_4$ (Liebig's method) $= 7.83$ per cent. S.

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[1] Loc. cit.

II. 0.12023 gram substance gave 0.06637 gram $BaSO_4$ (Liebig's method) = 7.58 per cent. S.

The substance contained water, and lost 14.08 per cent. in weight on heating for one hour at 125°–130°. On heating higher it continued to lose in weight. It seems probable that the loss at higher temperatures was due to partial decomposition, though this cannot be definitely stated. The facts established are not sufficient to warrant any speculation in regard to this compound. There is no serious difficulty involved in its preparation, and it is worthy of careful study.

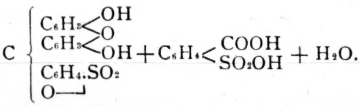
Another experiment, in which smaller quantities of dioxybenzoyl-benzene-sulphonic acid and sulphuric acid were used and a slightly lower temperature was maintained, was attended with practically the same results as the above. Analysis of the barium salt obtained gave 9.05 per cent. water, 36.65 per cent. barium. The substance similar to sulphon-fluoresceïn was considerably lighter in color than that above mentioned, but an estimation of sulphur gave 9 per cent., indicating the same composition.

Preparation of Sulphon-fluoresceïn from Dioxybenzoyl benzene-sulphonic Acid.

Sulphon-fluoresceïn was prepared from dioxybenzoyl-benzene-sulphonic acid by heating the latter in a sulphuric-acid bath at 160°–180°, stirring quite often during the operation. The conversion takes place readily, the melted acid soon acquiring a deep red-brown color. After two to two and a half hours, when the mass had become tolerably stiff, and the reaction seemed at an end, the heating was discontinued. After becoming cool the product was treated with cold water and filtered. The sulphon-fluoresceïn remaining on the filter was thoroughly washed with cold water, and then dissolved in moderately concentrated caustic potash. On adding dilute sulphuric acid it was precipitated in yellow flocculent masses, which quickly acquired a red-brown color. The precipitate was washed a few times by decantation, and finally on the filter with the aid of a pump. The nature of the precipitate is such that washing thoroughly on the filter is a matter of great difficulty.

Sulphon-fluoresceïn is very difficultly soluble in hot alcohol and in hot glacial acetic acid. It is apparently more easily soluble in hot water than in cold, though only slightly soluble in either. In the alkalies it is easily soluble, and the fluorescence of the alkaline solution is even more intense and beautiful than that of the alkaline solution of ordinary fluoresceïn. The amount of pure sulphon-fluoresceïn obtained from 40 grams of the acid was about 16 grams. The yield was tolerably satisfactory though not quantitative, the equation representing the conversion being doubtless the following:

$2(HO)_2C_6H_3.CO.C_6H_4.SO_2OH =$



$$C\left\{\begin{array}{l} C_6H_3<\begin{smallmatrix}OH\\O\end{smallmatrix} \\ C_6H_3<\begin{smallmatrix}\\OH\end{smallmatrix} \\ C_6H_4.SO_2 \\ O\text{—}\lrcorner \end{array}\right. + C_6H_4<\begin{smallmatrix}COOH\\SO_2OH\end{smallmatrix} + H_2O.$$

Analyses of Sulphon-fluoresceïn.

Complete analyses of sulphon-fluoresceïn confirm Remsen and Linn's results as to estimation of water and sulphur, and show conclusively that the actual composition of the substance is represented by $C_{19}H_{14}O_7S$, or $C_{19}H_{12}O_6S + H_2O$.

I. 0.07929 gram substance, heated for two hours at 125°-130°, lost 0.00374 gram H_2O.

II. 0.26414 gram substance gave 0.56943 gram CO_2 and 0.10215 gram H_2O.

III. 0.2634 gram substance gave 0.56994 gram CO_2 and 0.10157 gram H_2O.

IV. 0.17089 gram substance gave 0.10099 gram $BaSO_4$ (Liebig's method).

V. 0.12418 gram substance gave 0.07046 gram $BaSO_4$ (Liebig's method).

VI. 0.12877 gram substance gave 0.07299 gram $BaSO_4$ (Liebig's method).

VII. 0.12625 gram substance gave 0.07333 gram $BaSO_4$ (Liebig's method).

VIII. 0.12788 gram substance gave 0.07544 gram $BaSO_4$ (Liebig's method).

	Calculated for	Found.							
	$C_{19}H_{12}O_6S + H_2O$.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
H_2O	4.66	4.72	...	...	...	...	...	...	...
C	59.07	...	58.79	59.01	...	...	...	...	...
H	3.63	...	4.30	4.28	...	...	...	...	...
S	8.29	...	...	...	8.11	7.79	7.78	7.97	8.10

In all the sulphur estimations except the last Keiser's modification of the Liebig method was employed.[1] The original Liebig method usually gives high results, but as modified by Keiser the results obtained are usually close and are sometimes lower than the theoretical, hence the somewhat low figures obtained are not surprising.

Contributions from the Chemical Laboratory of the U. S. Department of Agriculture.

XXI.—THE CARBOHYDRATES OF THE COFFEE BERRY.

BY ERVIN E. EWELL.

(*Communicated by H. W. Wiley.*)

There are few more interesting or more important fields of work for the student of plant chemistry than the one now offered in the study of the substances that go to make up the sum-total of what analysts record as "nitrogen-free extract." The recent discoveries and investigations made in this line by Dr. Schulze at Zürich, Dr. Tollens at Göttingen, Dr. W. E. Stone of Purdue, and their collaborators, have led to much investigation in this direction.

In the search for material for study, the coffee-berry has not been entirely neglected. Mr. Walter Maxwell has demonstrated[2] the presence of a galactose-yielding body in the portion of coffee insoluble in water, and succeeded in preparing a considerable amount of pure and well crystallised galactose by hydrolysis of the water-insoluble residue with dilute sulphuric acid. Reiss[3] has reported the presence of a carbohydrate that yields mannose by hydrolysis. The water-soluble carbohydrates of coffee have received less attention, and indefinite statements concerning sugar, gum and dextrin make up the existing literature of the subject.

By experiments made in the laboratory of the Department of Agriculture, cane-sugar has been shown to be the principal carbohydrate soluble in water. It is accompanied by a small percentage of a substance resembling dextrin and a small percentage of some reducing sugar. The latter may result from a slight inversion of the cane-sugar before or during the process of extraction. Pure and well crystallised preparations of cane-sugar were obtained by two different methods. The first method used, for which we are indebted to Schulze, Steiger and Maxwell,[1] may be briefly outlined as follows: The finely ground material is extracted with 70 per cent. alcohol. This extract, after treatment with lead acetate and removal of the excess of lead with hydrogen sulphide, is precipitated at the boiling temperature of the liquid with excess of strontium hydroxide. The strontium saccharate thus formed is separated by filtration, suspended in water, and decomposed by a current of carbon dioxide. After filtration from the precipitated strontium carbonate, the solution is evaporated to a sirup, which is purified by repeated solution in alcohol, evaporation and resolution, gradually increasing the strength of the alcohol. The final solution in strong alcohol is left to crystallise. In the second method, the extract is evaporated to a sirup after treatment with lead acetate, and is then directly treated with alcohol without the use of strontium hydroxide. This method is shorter and yields as good results with the material in question as does the first method described.

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[1] This Journal **5**, 207.

[2] Private notes made accessible by kindness of Mr. Maxwell.

[3] Ber. d. chem. Ges. 1889, **22**, 609.

For the quantitative determination of the cane-sugar, 10 grams of coffee in 1 mm. powder were extracted in a continuous percolation apparatus with absolute ether, and the residue remaining was extracted with 75 per cent. alcohol. The extraction was continued until only a very indistinct reaction for sucrose was obtained by Seliwanoff's[2] resorcinol test. The final test was made by evaporating the entire extract obtained during a day's percolation and applying the test to a small portion of this concentrated solution. After removing the alcohol by evaporation, the united extracts were treated with basic lead acetate and diluted to a definite volume. After removal of the excess of lead and inversion in the usual manner, the sucrose was estimated in an aliquot part of the solution by means of Fehling's solution, determining the cuprous oxide electrolytically. Duplicate determinations gave 6.24 and

[1] Untersuchungen über die chemische Zusammensetzung einiger Legumenosensamen. Landwirt. Versuchs-Stationen, 1891, **39**, 269.

[2] Ber. d. chem. Ges., 1887, **20**, 181.

6.34 per cent. of sucrose. These numbers include the small amount of reducing sugar that was present.

The water-insoluble portion of coffee yields an abundance of furfuraldehyde when distilled with hydrochloric acid, sp. gr. 1.06, which indicates the presence of a pentose-yielding carbohydrate. By distillation of 5 grams of untreated coffee, 4.2-4.6 per cent. of furfuraldehyde were obtained, which is equivalent to 8-10 per cent. of a pentose (xylose or arabinose) in the original material. A gummy substance is obtained when a 5 per cent. sodium hydroxide extract is precipitated with alcohol according to the method used for the separation of xylan from wood.

When this gum is washed with alcoholic hydrochloric acid, alcohol and finally with ether, and is dried over sulphuric acid, a slightly grayish, translucent, hard and brittle mass is obtained, which is readily reduced to powder in a mortar. The properties of this substance were determined as far as the limited amount of material permitted. After hydrolysis with 5 per cent. sulphuric acid, it gave a reduction of Fehling's solution equivalent to 74.2 per cent. of dextrose; by distillation with hydrochloric acid, 13 per cent. of furfuraldehyde; by oxidation with nitric acid, 18.7 per cent. of mucic acid; and when burned, 0.84 per cent. of ash. While the small quantities of material used for these estimations precluded the desirable accuracy, the results obtained suggest a compound containing one galactose group and one pentose group. When the gum was inverted with dilute sulphuric acid, a slight flocculent residue remained. This is probably due to the slight and unavoidable turbidity of the sodium hydroxide extract and helps to account for the amount of reducing sugars obtained by hydrolysis of the gum.

Lintner and Düll[1] have reported a similar gum from barley. They found its hydrolysis product to contain equal numbers of molecules of galactose and xylose. Numbers obtained by elementary analysis agreed very closely with the theoretical percentages required by the formula $C_{11}H_{20}O_{10}$. They propose the name of "galactoxylan" for this substance. Lippmann[2] has separated a gum from sugar-beets that yields galactose and arabinose.

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[1] Über die chemische Natur des Gerstengummi. Zeitsch. f. angew. Chem., 1891, 538; Chem. Ztg. Repert., 1891, **15**, 266.

[2] Ber. d. chem. Ges. 1890, **23**, 3564; Zeitsch. f. angew. Chem. 1891, 538; Chem. Ztg. Repert. 1891, **15**, 44.

A separate portion of the water-insoluble material was hydrolysed with dilute sulphuric acid. By evaporation of the extract, after removal of the acid, a sirup was obtained that yielded an abundance of furfuraldehyde and mucic acid, showing that the pentose- and galactose-yielding substances were readily extracted by this reagent also.

The residue from the sucrose determination was heated on the steam-bath for 5 hours with 5 per cent. sulphuric acid. As the solution showed signs of darkening, it was removed from the bath at the end of this time. This strength of acid was used with the hope that the maximum amounts of pentose and galactose would be obtained, even if accompanied by a considerable amount of dextrose as a result of the partial hydrolysis of the cellulose. The extraction was incomplete, however, as the following data will show, since 4.2–4.6 per cent. of furfuraldehyde were obtained by distillation of the original material:

	Per cent. of the original material.
Reducing sugars (calculated as dextrose)	15.8
Mucic acid	5.7
Furfuraldehyde	2.6

These determinations have not been repeated under various conditions, in order to determine the proper strength of acid and length of time required for complete extraction.

Satisfactory evidence of any considerable amount of mannose in the sample of coffee used in this work has not been obtained. Parallel experiments were made with vegetable-ivory dust and coffee. With the former, an abundance of mannose-phenylhydrazon was obtained; with coffee, the slight precipitate obtained was dark-colored and insufficient in amount for a determination of its properties. The quantitative data obtained do not leave room for more than a small percentage of mannose.

LABORATORY OF THE U. S. DEPT. OF AGRICULTURE, *June* 22, 1892.

NOTES.

Carl Schorlemmer.

Carl Schorlemmer, LL. D., F. R. S., Professor of Chemistry in the Owens College, Manchester, died June 27, 1892, in his fifty-ninth year. A native of Darmstadt, his first work in chemistry was carried on in that city, and afterwards in Giessen. In 1858 he became assistant to Professor Roscoe, in the Owens College, and it is with this institution that his name has always been associated. With Roscoe he continued the work commenced by the former with the assistance of Dittmar, upon the composition of the aqueous acids. In 1861 his attention was called to the light oils produced by the distillation of cannel coal, and this led to the famous series of investigations upon the constitution of the paraffins. It will suffice to say that to a great extent we owe to him our present conception of the relations which the individual members bear to one another. Starting with the halogen derivatives of methane, he prepared its homologues successively by synthetical methods and showed them to be identical with the hydrocarbons derived from natural sources. In referring to the work by which he established the identity of dimethyl with "ethyl hydride," of "ethylpentyl" with "heptyl hydride," of "diamyl" with "decyl hydride," Sir Henry Roscoe says: "It is difficult to overestimate the importance of this apparently simple discovery. It laid forever the ghost of the existence of two sets of isomeric hydrocarbons of the paraffin series, and paved the way for Kekulé's theory of carbon combination, upon which the whole modern theory of organic chemistry is based. So to Schorlemmer belongs the credit of placing in position the foundation-stone of our science."

As an author Schorlemmer was equally distinguished. In addition to his text-books of the Chemistry of Carbon Compounds, he is everywhere known as the co-author, with Roscoe, of their great "Treatise on Chemistry," published simultaneously in England and in Germany. The section of this work devoted to the carbon compounds has been almost entirely prepared by Schorlemmer, and his death will make it necessary for another to finish the work he had brought almost to completion.

Professor Roscoe speaks of a History of Chemistry upon which Schorlemmer was engaged at the time of his death, and which he had completed down to the close of the eighteenth century. The publication of this work is promised and will be looked for with interest.

W. W. R.

Iodosobenzoic Acid.

Victor Meyer and W. Wachter give in the *Berichte*[1] an account of the preparation of what appears to be an idosobenzoic acid, $C_6H_4{<}\genfrac{}{}{0pt}{}{I=O}{CO.OH}$, in which the atom of iodine plays the same rôle as the atom of nitrogen in the corresponding nitroso compound. Orthoiodobenzoic acid is dissolved in fuming nitric acid; a reaction evidently takes place, and, on addition of water, the new compound separates out. When the deposition takes place slowly the product is crystalline. It contains no nitrogen, but the amount of oxygen is half again as great as in iodobenzoic acid. The new compound melts at 209° with decomposition; orthoiodobenzoic acid melts without decomposition at 162°. The new acid is a strong oxidising agent; when brought together with potassium iodide, in the presence of a little sulphuric acid, iodine is set free in quantitative amount—

$$C_6H_4(IO).CO.OH + 2HI = C_6H_4I.CO.OH + H_2O + I_2.$$

On heating the acid with concentrated hydrochloric acid, chlorine is evolved. The other product in each case is orthoiodobenzoic acid. When the compound is dissolved in ammonia and treated with zinc-dust, benzoic acid is produced—a reaction characteristic of iodobenzoic acid also. The acid dissolves in the alkalies and is reprecipitated on addition of acids. If to the solution in ammonia silver nitrate be added, a precipitate of *pure iodosobenzoic acid* is produced.

No similar compound could be obtained from the corresponding chlor- and brombenzoic acids; which fact leads the authors to conclude that the third oxygen atom is held in place through some peculiarity of the iodine atom. This oxygen is not directly connected with the benzene nucleus, for under such conditions an hydroxybenzoic acid should be formed through the action of nascent hydrogen. As a matter of fact benzoic acid is the product of this action.

With aniline and with orthoamidobenzoic acid iodosobenzoic acid reacts with the formation of a product closely resembling the azo compounds; this may contain the grouping $-N=I-$, corresponding to that of the azo derivatives, $-N=N-$.

Idosobenzoic acid decolorises potassium permanganate solution. In this way an acid $C_6H_4{<}\genfrac{}{}{0pt}{}{IO_2}{CO.OH}$ may perhaps be produced. The authors have also found that on treating benzene with a mixture of sulphuric and *iodic* acids, a crystalline product is obtained. This product had not at the time of publication of this paper been examined. The analogy with the reaction by which nitro compounds are formed leads them to suspect that the product is an iodobenzene, $C_6H_n(IO_2)_{6\ n}$. The investigation of this and similar reactions is now in progress. With respect to the corresponding meta- and paraiodobenzoic acids the authors state that no similar compound is formed by the action of nitric acid.

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[1] Ber. d. chem. Ges. **25**, 2632.

It may be noted in passing that we have not, as the Germans have, names which will distinguish between the compounds $C_6H_4.I.CO.OH$ and $C_6H_4(IO_2)CO.OH$, etc., should members of the latter class be prepared. Meyer applies the name iodobenzoic acid to the second of the two substances whose formulæ are given above.

W. W. R.

The Preparation of Hydrazoic Acid.

A new method for the preparation of hydrazoic acid, which does not involve the use of organic compounds of nitrogen, is described by W. Wislicenus,[1] and is based upon the fact that nitrous oxide reacts upon sodamide in accordance with the following equation:

$$2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3.$$

The method of procedure is as follows: Metallic sodium in small pieces is placed in a large porcelain boat and the latter inserted in a piece of combustion-tubing heated by means of a combustion-furnace. Dry ammonia is passed over the melted sodium until it has been entirely converted into sodamide. The temperature is then allowed to fall to 150°–250°, and dry nitrous oxide is substituted for the ammonia. This part of the experiment may advantageously be conducted with the tube in a Carius furnace. The mass puffs up and continues to evolve ammonia until the sodamide is completely decomposed. If a *mixture* of ammonia and nitrous oxide be passed over the melted sodium, the same reaction takes place, but the yield is not so good; in addition to this, the reaction of sodium with nitrous oxide at times produces undesirable results. The same reaction takes place in the case of potassamide, KNH_2, and of zincamide, $Zn(NH_2)_2$; in the case of zincamide the yield is poor. In each case the corresponding salt of hydrazoic acid is formed. This is dissolved in water, the solution filtered, mixed with dilute sulphuric acid, and distilled. A solution of pure hydrazoic acid collects in the receiver. The aqueous acid gives the characteristic precipitates with silver, lead and mercurous salts, dissolves gold-dust, etc.,—in short, exhibits all the properties described by Curtius.[2]

W. W. R.

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[1] Ber. d. chem. Ges. **25**, 2084.

[2] This Journal **12**, 587; **13**, 284.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. Beckurts, R. Benedikt, C. A. Bischoff, E. A. Dürre, J. M. Eder, E. Valenta, C. Häussermann, G. Krüss, M. Märcker, L. Bühring, W. Nernst, und F. Röhmann, herausgegeben von Richard Meyer. I Jahrgang. 1891. H. Bechold, Frankfurt a. M., 1892. x + 544 pp. 8vo.

The object of this publication is not to supplant the old Jahresbericht, but to present the principal results of investigations in all branches of pure and applied chemistry quickly and in readable form. There is unquestionably room for it, and many who groan under the enormous weight of current chemical literature will welcome it as a friend in need. Even the conscientious reader of the journals will find it a help, for the specialists who prepare these reports will no doubt see things that escape the ordinary reader. One cannot keep in touch with every kind of work. He who is interested in physical chemistry will, in his reading, be apt to neglect organic chemistry to some extent, and *vice versa*. Now, by the aid of the Jahrbuch der Chemie, we shall be able at the end of the year to make up our deficiencies, or at least to see where our deficiencies are. Every chemist will find the book useful. It covers a large field, including reports on (1) Physical Chemistry; (2) Inorganic Chemistry; (3) Organic Chemistry; (4) Physiological Chemistry; (5) Pharmaceutical Chemistry; (6) Chemistry of Foodstuffs; (7) Agricultural Chemistry; (8) Metallurgy; (9) Inorganic Chemical Technology; (10) Explosives; (11) Technology of the Carbohydrates and Fermentation Industries; (12) Technology of Fats; (13) Chemistry of Tar and Dyes; (14) Photography. The reports are written by chemists specially qualified for the work, and the work bears every evidence of having been done with care. Special mention should be made of the report on Physical Chemistry by W. Nernst; that on Inorganic Chemistry by G. Krüss; that on the Chemistry of Tar and Dyes by R. Meyer, and that on Photography by J. M. Eder and E. Valenta. This volume, which covers the work done in Chemistry in 1891, was published early in 1892. An equally prompt publication of the succeeding volumes is promised, the editor having adopted the motto *Bis dat qui cito dat!* I. R.